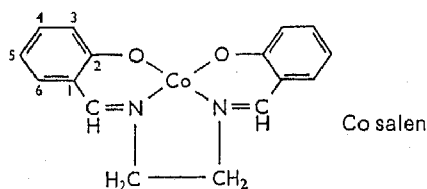


## Oxygen Adducts of Schiff's Base Complexes of Cobalt Prepared in Solution

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Some 1:2 adducts of oxygen with *NN'*-ethylenebis(salicylideneiminato)cobalt(II), Co salen, and its ring-substituted analogues are reported. These compounds, which were obtained from solutions of the cobalt(II)-Schiff's base complexes, were found to be substantially diamagnetic from room temperature to 90°K. The magnetic susceptibility of the 1:2 adduct of oxygen with Co salen obtained by the solid-state reaction has been measured from room temperature to 90°K: it is concluded that, when allowance is made for small impurities of unconverted Co salen, this product is substantially diamagnetic. Finally, conditions have been found in which Co 3-methoxysalen gives a 1:1 adduct with oxygen in pyridine as solvent. I.r. and magnetic susceptibility data suggest that the oxygen group in this adduct of formula Co 3-methoxysalen,py,O<sub>2</sub> is symmetrically bonded to cobalt in an ethylene-like type of arrangement.

THE oxygen-carrying properties of *NN'*-ethylenebis(salicylideneiminato)cobalt(II), hereinafter Co salen, were



recognised by Tsumaki,<sup>1,2</sup> Calvin and his co-workers later studied the oxygenation of Co salen, particularly

Conditions under which a complex having a Co salen-type of structure forms a 1:1 adduct have also been identified.

### RESULTS AND DISCUSSION

**1:2 Adducts.**—Co salen and its ring-substituted derivatives have been found to absorb oxygen in aprotic solvents giving rise to adducts in which the oxygen:cobalt ratio is 1:2. The compounds obtained (I—VI) are presented in Table 1, together with some of their properties.

TABLE 1  
Oxygen adducts of Co salen and its ring-substituted derivatives

Compound <sup>a</sup>	Colour	10 <sup>6</sup> χ <sub>m</sub> <sup>b</sup> (c.g.s.u.)	10 <sup>6</sup> × dia- magnetic correction/ mole (c.g.s.u.) <sup>c</sup>	μ <sub>eff</sub> <sup>b,c</sup> (B.M.)
(Co salen) <sub>2</sub> O <sub>2</sub> (DMF) <sub>2</sub> (I)	Black	196	212	0.7
(Co salen) <sub>2</sub> O <sub>2</sub> (DMSO) <sub>2</sub> (II)	Black-brown	261	211	0.8
(Co salen) <sub>2</sub> O <sub>2</sub> (pyO) <sub>2</sub> (III)	Black	148	221	0.6
(Co salen) <sub>2</sub> O <sub>2</sub> py <sub>2</sub> (IV)	Red-brown	129	216	0.5
(Co 3-methoxysalen) <sub>2</sub> O <sub>2</sub> (DMSO) (V)	Black	387	221	1.0
(Co 5-chlorosalen) <sub>2</sub> O <sub>2</sub> (DMSO) <sub>2</sub> (VI)	Red-brown	388	245	1.0
Co 3-methoxysalen,py,O <sub>2</sub> (VII)	Red-brown	1147	239	1.65

<sup>a</sup> In the Tables and throughout the text the following abbreviations are used: DMA (dimethylacetamide), DMF (dimethylformamide), DMSO (dimethyl sulphoxide), py (pyridine), pyO (pyridine oxide), diglyme (2,2'-dimethoxydiethyl ether), THF (tetrahydrofuran). <sup>b</sup> At 296°K. <sup>c</sup> Per cobalt atom.

in the solid state. Active forms of Co salen, capable of absorbing oxygen in the solid state, were obtained<sup>3</sup> by removing the pyridine *in vacuo* at high temperature from the pyridine adduct Co salen,py. We have reported<sup>4</sup> the preparation of oxygen adducts of Co salen in aprotic solvents such as dimethylformamide and dimethyl sulphoxide.

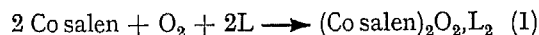
We now report the properties of these adducts and others obtained from the same quadridentate Schiff's base but with substituents in positions of the aromatic ring. We have also carried out an investigation of the factors, particularly solvent and ligand environment, influencing the formation of oxygen adducts of Co salen.

<sup>1</sup> T. Tsumaki, *Bull. Chem. Soc. Japan*, 1938, **13**, 252.

<sup>2</sup> For a review on synthetic oxygen carriers see L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, 1963, **63**, 269.

<sup>3</sup> R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

Consider the oxygen adducts of Co salen first. The oxygenation occurs according to the stoichiometry (I)



in which L represents a molecule of solvent or, more generally, a ligand capable of occupying a co-ordination position around the metal. When L is dimethylformamide or dimethyl sulphoxide the oxygen adducts have been isolated pure and analysed. The oxygen:cobalt ratio was checked not only by direct elemental analysis but also by gas-volumetric measurements of the oxygen absorbed (Table 2). The preparation of the oxygen adducts of Co salen from solution was expected to offer certain advantages over the solid-state reaction of active Co salen with oxygen, as reported by Bailes and Calvin.<sup>3</sup>

<sup>4</sup> F. Calderazzo, C. Floriani, and J.-J. Salzmann, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 379.

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Calvin and his co-workers<sup>3,5</sup> had indicated the formation of an oxygen adduct in pyridine but no further investigation of the behaviour of Co salen towards oxygen in solution has appeared.

The formation of 1:2 oxygen adducts of Co salen is usually a rather fast process especially when the reaction is carried out from suspension, as is the case for most of the runs of Table 2.<sup>6</sup> It is noteworthy that only a few solvents can promote the oxygenation of Co salen. The best are dimethylformamide and dimethyl sulphoxide. The following solvents were tried unsuccessfully: toluene, chloroform, acetone, tetrahydrofuran,

In general, some kind of stabilisation of the oxygen adducts by the ligand L has to be considered. While steric factors may be responsible for the failure of some of the solvents mentioned to promote the oxygenation (for example, dimethylacetamide as opposed to dimethylformamide), electronic effects should largely determine the possibility for certain ligands to stabilise the metal-oxygen bond. The substances which have been found to promote the oxygenation of Co salen are ligands whose  $\pi$ -acceptor properties are non-existent or very small. We shall assume that the co-ordination around the cobalt in these 1:2 adducts is that depicted in Figure 1, in

TABLE 2  
Gas-volumetric oxygen absorption on Co salen, its derivatives, and Co salPr

Compound (mmoles)	Solvent <sup>a</sup> (ml.)	Ligand (mmoles)	Temp.	O <sub>2</sub> absorbed (mmoles)	Ratio O <sub>2</sub> :Co
Co salen (1.025)	DMF (40)	—	12.0°	0.515	0.50
Co salen (1.382)	py (40)	—	13.0	0.659	0.48
Co salen (1.868)	DMA (35)	pyO (7.57)	12.0	0.889	0.48
Co salen (1.235)	Diglyme (25)	SCN <sup>-</sup> (7.85)	12.0	0.647	0.52
Co salen (0.957)	DMA (35)	N <sub>3</sub> <sup>-</sup> (16.92)	12.0	0.466	0.49
Co salen (1.382)	DMA (37)	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> (30.56)	12.0	0.731	0.53
Co 3-methoxysalen (1.713)	DMSO (35)	—	28.0	0.768	0.45
Co 5-chlorosalen (1.577)	DMSO (35)	—	27.5	0.714	0.45
Co 5-chlorosalen (0.912)	py (30)	—	12.5	0.429	0.47
Co salPr (0.610)	THF (20)	—	14.1	0.670	1.10
Co salPr (0.717)	CHCl <sub>3</sub> (30)	—	14.5	0.783	1.10
Co salPr (0.723)	DMF (20)	—	9.3	0.504	0.70
Co salPr (0.729)	py (20)	—	14.1	0.988	1.35
Co salPr (0.598)	Toluene (20)	—	14.2	0.288	0.48
Co 3-methoxysalen (1.539)	py (30)	—	10.4	1.404	0.91

<sup>a</sup> In the runs with Co salen and its derivatives the volume of solvent used was not sufficient to assure complete dissolution of the cobalt complex.

2,2'-dimethoxydiethyl ether (diglyme). In dimethylacetamide the formation of the oxygen adduct can also be regarded as unsuccessful although small amounts of oxygen were found to be absorbed during long reaction times. The negative results obtained with such a large variety of representative solvents, combined with the fact that the solvent molecules are found as ligands to the cobalt in the final reaction products, indicate that the solvent not only brings Co salen into contact with dissolved oxygen, but also provides a favourable path for the reaction.

In addition to the oxygenations in 'active' solvents, we found that the presence of certain ligands promotes the oxygenation of Co salen in usually inert solvents. Beside pyridine oxide, some anionic ligands were effective, namely SCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>. These reactions were carried out in non-aqueous aprotic solvents. Although product isolation was not attempted with the anionic ligands, the gas absorption was measured and found to correspond, within experimental error, to the formation of the 1:2 adducts (Table 2). It is believed that oxygen adducts of composition [(Co salen)<sub>2</sub>O<sub>2</sub>L<sub>2</sub>]<sup>2-</sup> are formed in these cases, in which L represents one of the anionic ligands.

which the oxygen and the additional ligand occupy the axial positions of an idealised octahedral configuration. It appears that the role of the ligand *trans* to oxygen is that of compensating the charge transferred from cobalt to oxygen. In other words, the presence of  $\sigma$ -donors would stabilise the metal-oxygen bond. This explanation is similar to that given<sup>6</sup> in the case of

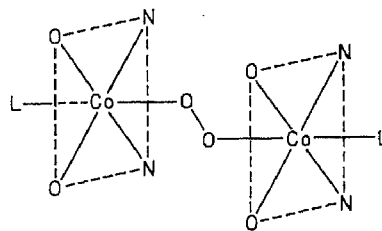


FIGURE 1 Schematic idealised structure of 1:2 oxygen adducts of the type (Co salen)<sub>2</sub>O<sub>2</sub>L<sub>2</sub>

IrI(CO)(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub> in order to account for both the irreversibility of this oxygen adduct and the larger oxygen-oxygen distance than in the corresponding chloro-derivative.<sup>7</sup>

The oxygen adducts of Co salen containing dimethylformamide (I), dimethyl sulphoxide (II), and pyridine oxide (III) readily lose the combined molecular oxygen either by heating *in vacuo* at about 80° or by treatment

<sup>7</sup> S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581.

<sup>5</sup> M. Calvin, R. H. Bailes, and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1946, **68**, 2254.

<sup>6</sup> J. A. McGinney, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 2243.

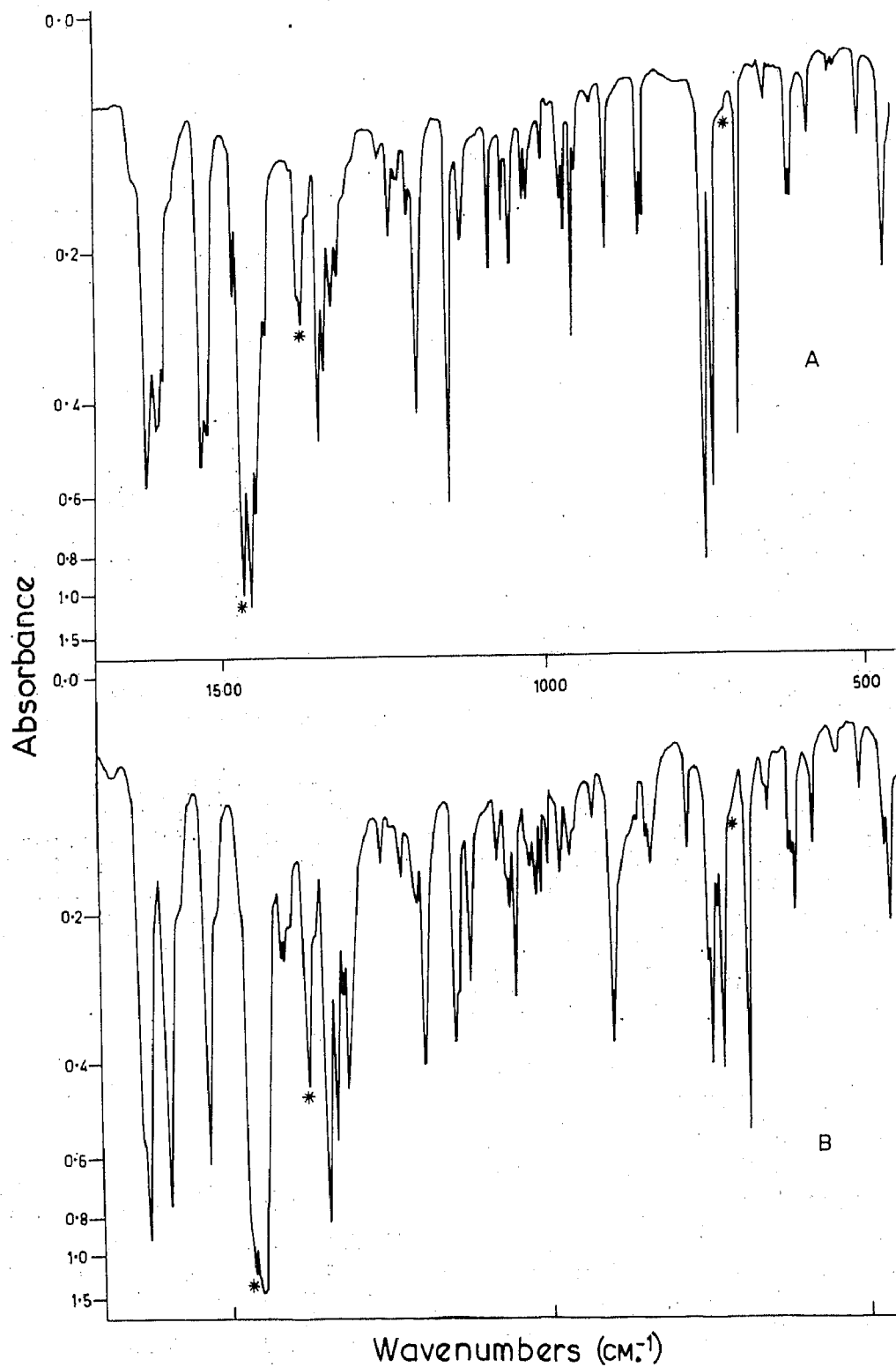


FIGURE 2 Infrared spectra between 1300 and 450  $\text{cm}^{-1}$  (Nujol mulls): A,  $\text{Co(salen),py}$ ; B,  $(\text{Co(salen)}_2)\text{O}_2,\text{py}_2$ . Bands marked with an asterisk are due to Nujol.

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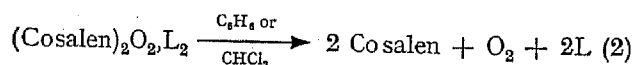
<sup>9</sup> B. Bo

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<sup>10</sup> M. Ca

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with benzene or chloroform. Ueno and Martell<sup>8</sup> mentioned that the oxygen adduct of Co salen prepared by the solid-state reaction evolves oxygen in the presence of chloroform. We have verified this and found that the oxygen evolution is quantitative. Reaction (2) was used for the quantitative determination of the combined molecular oxygen in the above mentioned adducts.



Reaction (2), also provides an easy and reliable criterion for the reversibility of the oxygenation, but it cannot always be carried out successfully. For example, the pyridine derivative  $(\text{Co salen})_2\text{O}_2 \cdot \text{py}_2$  is only partially decomposed by benzene or chloroform for reasons which are not clearly understood. We could, however, exclude that this compound contains some of the pyridine oxide complex  $\text{Co salen, pyO}$  which would have the same analytical composition. We have in fact verified that  $\text{Co salen, pyO}$  is not stable in the presence of oxygen and gives the oxygen adduct (III). The latter, as mentioned above, releases quantitatively the combined oxygen on treatment with benzene or chloroform.

The i.r. spectrum of the 1:2 adduct (IV) compared with the unconverted  $\text{Co salen, py}$  is reported in Figure 2. No strong new band attributable to the  $\text{O}_2$  group is observed. This is in agreement with the structure indicated in Figure 1 because such a symmetrical arrangement would lead to a substantially i.r.-inactive O-O stretching vibration.<sup>9</sup> In agreement with the results of Ueno and Martell<sup>8</sup> the oxygen adduct has a new weak band at about  $500 \text{ cm}^{-1}$ .

Substitution with a methoxy- or a chloro-group in positions 3 and 5, respectively, of the aromatic ring of Co salen causes some important modifications in the properties of the corresponding oxygen adducts. One substantial difference concerns their lability in the presence of chloroform or benzene. While the quantitative release of oxygen upon contact with benzene or chloroform indicated a rather labile metal-oxygen bond in compounds (I), (II), (III), and in the solid state adduct  $(\text{Co salen})_2\text{O}_2$ , the 5-chloro-derivative (VI) is completely unaffected under the same conditions and only partial release of oxygen is obtained in the case of the 3-methoxy-derivative (V). The ring-substituted derivatives, however, release oxygen upon heating *in vacuo*. The recovery of the starting cobalt(II) complexes excluded the possibility that we were dealing with an irreversible oxidation rather than with an oxygenation.

**Magnetic properties.** Calvin and Barkelew<sup>10</sup> reported that the molar magnetic susceptibility of active Co salen decreased on formation of the 1:2 oxygen adduct up to a minimum value of 160 c.g.s.u. at room temperature.

<sup>8</sup> K. Ueno and A. E. Martell, *J. Amer. Chem. Soc.*, 1956, **80**, 1270.

<sup>9</sup> B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1514.

<sup>10</sup> M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267.

We have measured the magnetic susceptibility of an oxygen adduct of formula  $(\text{Co salen})_2\text{O}_2$  prepared in the solid state from active Co salen and confirmed that  $\chi_M$  at room temperature is rather small (239 c.g.s.u., corresponding to an apparent  $\mu_{\text{eff}}$  0.7 B.M.). A temperature-dependence study between 90 and 296°K showed that the magnetic susceptibility varied with the temperature and followed the Curie-Weiss law quite closely (see Experimental section). The most reasonable interpretation of these results is that small amounts of unconverted Co salen were contained in the sample, despite the long reaction time and all the precautions taken. The active form of Co salen is known<sup>11</sup> to follow the Curie-Weiss law with  $\theta = 25^\circ$ . On the other hand, the type of temperature-dependence of  $\chi_M$  exclude that strong anti-ferromagnetic coupling is responsible for the low magnetic moment of Calvin's oxygen adduct. The latter, in view of the present magnetic data, has to be regarded as a normal diamagnetic substance, eventually with a residual temperature-independent paramagnetism. The latter is indicated by the magnetic susceptibility measurements on the oxygen adducts (I), (II), and (VI) prepared from solution. No important contamination of unconverted Co salen is found in these products, as expected. The small positive magnetic susceptibility found can be assigned to temperature-independent paramagnetism, as indicated by the plot of  $\mu_{\text{eff}}$  against  $T^{1/2}$  (Figure 3). No unpaired spin is therefore present in these oxygen adducts which, therefore, have magnetic properties very similar to those of the nitrogen oxide adducts of Co salen and its ring-substituted derivatives.<sup>12</sup>

Under certain conditions, especially by carrying out the preparation from dilute solutions, the oxygen adduct (II) shows much higher values of  $\chi_M$ . Temperatures and values of  $\chi_M$  (in parentheses) are given here for a typical sample of this 'high moment' derivative at a magnetic field of 10,400 Oe: 90°K (836 c.g.s.u.); 120 (785); 150 (784); 180 (761); 210 (797); 240 (763); 295 (712). The preparation of this magnetically anomalous derivative, which is analytically identical with the more frequent normal form, is not reproducible. Further, the magnetic susceptibilities observed depend on the magnetic field. We interpret this as being due to the presence of small amounts of ferromagnetic impurities in the sample. This sets an example of the precautions which must be taken in interpreting magnetic data in this type of compound.

The pyridine oxide derivative (III) and  $(\text{Co salen})_2\text{O}_2 \cdot \text{py}_2$  (IV) have small magnetic susceptibilities at room temperature (see Table 1). There is no reason to believe that these compounds are magnetically different from all the others. The 3-methoxy-derivative (V) is also practically diamagnetic at room temperature.

<sup>11</sup> (a) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 338; (b) B. N. Figgis and J. Lewis, 'The Magnetic Properties of Transition Metal Complexes,' in 'Progress in Inorganic Chemistry,' ed. F. A. Cotton, Interscience Publ., New York, N.Y., vol. 6, p. 193.

<sup>12</sup> A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *J. Chem. Soc.*, 1965, 4718.

The results of the magnetic investigation on the oxygen adducts of this class tend to suggest a peroxide type of bonding of originally  $d^7$  low-spin cobalt with oxygen. Formally, a transfer of two electrons would take place to the antibonding orbitals of oxygen through the intermediacy of the cobalt atoms. The bidentate peroxide ion co-ordinates to cobalt through donation of lone-pairs on the oxygens into empty  $d$  orbitals of the metal.

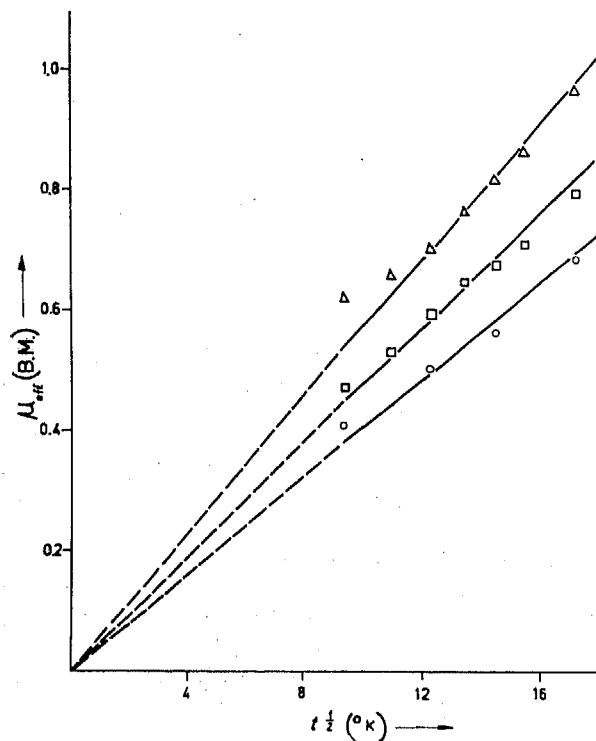
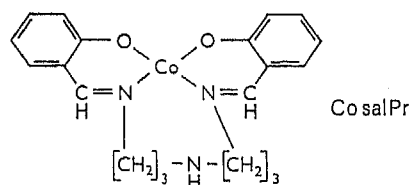


FIGURE 3 Plot of  $\mu_{\text{eff}}$  against  $T^{1/2}$  for some 1:2 oxygen adducts of Co salen derivatives.  $\circ$   $(\text{Co salen})_2\text{O}_2(\text{DMF})_2$ ,  $\square$   $(\text{Co salen})_2\text{O}_2(\text{DMSO})_2$ ,  $\Delta$   $(\text{Co 5-chlorosalen})_2\text{O}_2(\text{DMSO})_2$

This type of bonding should result in an arrangement as depicted in Figure 1.

A similar type of arrangement has recently been found for the oxygen-bridged pentamminecobalt cation.<sup>13</sup>

**1:1 Adducts.**—Bailes and Calvin<sup>3</sup> reported that *NN'*-imino-di-*n*-propylbis(salicylideneiminato)cobalt(II), hereinafter Co salPr, absorbed oxygen in the solid state up to a weight increase corresponding to the formation of a 1:1 adduct or slightly higher. Fritz and Gretner<sup>14</sup>



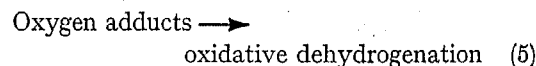
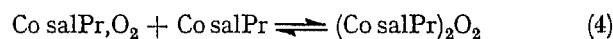
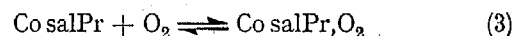
recently found, on the other hand, some evidence for the formation of a 1:2 adduct of Co salPr in solution.

<sup>13</sup> W. P. Schaefer and R. E. Marsh, *J. Amer. Chem. Soc.*, 1966, **88**, 178.

<sup>14</sup> H. P. Fritz and W. Gretner, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 141.

We have obtained new results which throw some light on this problem. As indicated in Table 2, CoSaPr during long reaction times absorbs oxygen in variable amounts depending on the solvent used. Values of the  $\text{O}_2$ :Co ratios between 0.5 and 1.0 can probably be explained by equilibria being set up under the experimental conditions. Some facts deserve, however, some comments. In toluene a value very close to 0.5 was obtained for the  $\text{O}_2$ :Co ratio even during very long reaction times. This shows that the solid precipitated under these conditions is the 1:2 adduct. However, in more polar solvents, in which no precipitation of solid products was observed, the oxygen absorption went beyond the value corresponding to the formation of the 1:2 adduct. In tetrahydrofuran, a solid analysing correctly for  $\text{Co salPr}_2\text{O}_2$  was isolated. Although this formulation is supported also by the gas-volumetric measurement, it cannot be excluded that some small alteration of the organic ligand has occurred. This is suggested by the observation that in pyridine the oxygen absorption went appreciably beyond the value expected for the formation of a 1:1 adduct. This could correspond to a partial oxidative dehydrogenation of the  $-\text{[CH}_2\text{]}_3-\text{NH[CH}_2\text{]}_3-$  bridge of Co salPr. A dehydrogenation of a similar type was found<sup>15</sup> to occur in the case of an aliphatic quadri-dentate  $\alpha$ -amine oxime complex of cobalt.

In view of the present results we suggest a tentative scheme (3), (4), (5) for the oxygenation of CoSaPr in solution, in which we assume that the 1:1 adduct is



formed first in a slow step and that in a second faster step the formation of the binuclear complex occurs. A second assumption is that the constant of equilibrium (4) is rather small. In a poor solvent such as toluene, on the other hand, the equilibrium is shifted towards the formation of the less soluble 1:2 adduct. In better solvents such as tetrahydrofuran or chloroform the concentration of the 1:1 adduct can increase up to the values required by the equilibria involved. In the scheme suggested, the preliminary formation of the 1:1 adduct is in agreement with a recent kinetic study<sup>16</sup> of the oxygenation of bis(histidinato)cobalt(II).

Whereas the behaviour of Co salPr towards oxygen in solution seems to be rather complicated, we succeeded in isolating what we believe to be the first well authenticated example of a 1:1 adduct of a cobalt Schiff's base complex with oxygen. We have in fact found that pyridine solutions of Co 3-methoxysalen undergo oxygen absorption and the compound obtained by this reaction corresponds to the formula  $\text{Co 3-methoxysalen,py}_2\text{O}_2$  (see

<sup>15</sup> F. G. Vassian and R. K. Murrmann, *Inorg. Chem.*, 1967, **6**, 2043.

<sup>16</sup> J. Semplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1967, **89**, 6092.

Tables 2 and 3). The formation of the oxygen adduct appears to be reversible since upon heating *in vacuo* the starting cobalt complex can be recovered. The magnetic moment, which approximately corresponds to one unpaired electron, is not in contradiction with regarding Co 3-methoxysalen,py,O<sub>2</sub> as a low-spin octahedral complex of cobalt(II). The rather low value of magnetic moment may be due to some contamination from the 1:2 adduct. The most reasonable theory concerning 1:1 metal complexes to oxygen has been put forward by Griffith.<sup>17</sup> He regards oxygen as being

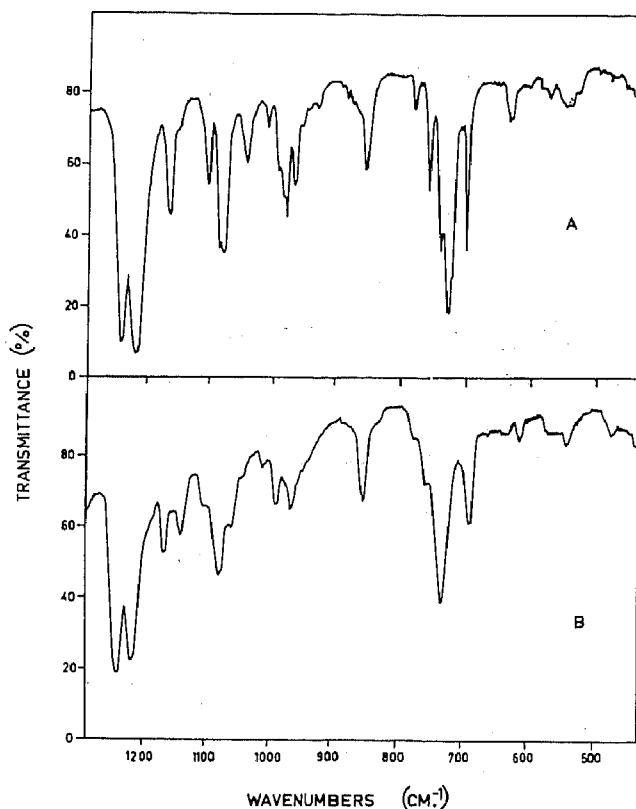


FIGURE 4 Infrared spectra between 1300 and 450 cm.<sup>-1</sup> (Nujol mulls): A, Co 3-methoxysalen,py; B, Co 3-methoxysalen,py,O<sub>2</sub>

bonded to metals in an excited singlet state closely resembling ethylene. Bonding would then occur from a  $\pi$ -orbital of oxygen to an empty *d*-orbital of the metal. Back donation is also possible by making use of empty antibonding orbitals on oxygen.

The i.r. spectrum of Co 3-methoxysalen,py,O<sub>2</sub> is shown in Figure 4 in comparison with the spectrum of unconverted Co 3-methoxysalen,py. The similarity of the two spectra is remarkable and the oxygen adduct has only

<sup>17</sup> J. S. Griffith, *Proc. Roy. Soc.*, 1956, *A*, 235, 23.

<sup>18</sup> L. Vaska, *Science*, 1963, **140**, 809.

<sup>19</sup> P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

<sup>20</sup> J. A. McGinety, R. J. Doedens, and J. A. Ibers, *Science*, 1967, **155**, 709.

<sup>21</sup> C. D. Cook and G. S. Jauhal, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 31.

<sup>22</sup> G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, 1967, **79**, 62.

a new rather weak band at about 1140 cm.<sup>-1</sup> and possibly another one at 1060 cm.<sup>-1</sup>. The former band can be assigned tentatively to the O-O stretching vibration of the oxygen ligand. This vibration which is i.r.-inactive in the isolated molecule may become i.r.-active when oxygen is bonded to the metal because of loss of symmetry. The failure to observe strong absorption bands due to oxygen in the i.r. spectrum of Co 3-methoxysalen,py,O<sub>2</sub> contrasts with the finding that other 1:1 oxygen adducts such as IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>,<sup>18,19</sup> IrI(CO)(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>,<sup>19,20</sup> Pt(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>,<sup>21,22</sup> Pd(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>,<sup>21</sup> Ni(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>,<sup>22</sup> and [RhCl(PPh<sub>3</sub>)O<sub>2</sub>]<sub>n</sub><sup>23</sup> all show a strong absorption between 800 and 900 cm.<sup>-1</sup> which has been attributed to the O-O stretching vibration of the oxygen group. This assignment has been, however, recently questioned<sup>20</sup> on the basis that the chloro- and iodo-derivatives IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub> and IrI(CO)(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub> have an almost identically located band (858 and 862 cm.<sup>-1</sup>, respectively) although the O-O distance differ by almost 12%. A recent i.r. study<sup>24</sup> of the isocyanide-oxygen complexes of nickel and palladium M(RNC)<sub>2</sub>O<sub>2</sub> using <sup>18</sup>O<sub>2</sub> appears to confirm that the band at 800-900 cm.<sup>-1</sup> can be assigned to the O-O stretching vibration.

We believe that the absence of a strong absorption due to the oxygen group in Co 3-methoxysalen,py,O<sub>2</sub> supports the view that the two oxygen atoms are symmetrically arranged with respect to the metal. This amounts to saying that, by considering O<sub>2</sub> as a unidentate ligand, we are dealing with a hexaco-ordinate complex in which the oxygen-oxygen bond is parallel to the plane defined by the two nitrogen atoms and the two oxygen atoms of the Schiff's base dianion.

#### EXPERIMENTAL

The magnetic susceptibilities were measured with a magnetic balance of the Gouy type between 90°K and room temperature at field strengths ranging from 3200 to 11,000 oersted. We thank Dr. E. Mooser of this Institute for permission to use the balance and for advice on its use. The temperature control was obtained by balanced evaporation of liquid nitrogen and heating of a copper tube surrounding the sample. The deviations were  $\pm 0.1^\circ$  over the whole temperature range. The balance was calibrated with CuSO<sub>4</sub>·5H<sub>2</sub>O<sup>25</sup> and HgCo(NCS)<sub>4</sub>.<sup>11a</sup> The values of magnetic susceptibilities are believed to be accurate to within 2%. The diamagnetic corrections for the organic ligands and for cobalt were taken from the literature<sup>26</sup> or calculated by use of Pascal's constants.<sup>27</sup> The i.r. spectra were measured with Perkin-Elmer 521 (Figure 2) and 337 spectrophotometers (Figure 4) equipped with a grating.

All the starting cobalt complexes were prepared under

<sup>23</sup> J. Blum, H. Rosenman, and E. D. Bergmann, *Tetrahedron Letters*, 1967, 3665.

<sup>24</sup> K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Comm.*, 1968, 533.

<sup>25</sup> B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 331.

<sup>26</sup> G. Foëx, 'Constantes sélectionnées, diamagnétisme et paramagnétisme,' Masson et Cie, Paris, 1957.

<sup>27</sup> B. N. Figgis and J. Lewis, 'The Magnetochemistry of Complex Compounds,' in 'Modern Co-ordination Chemistry,' ed. J. Lewis and R. G. Wilkins, Interscience, New York, N.Y., 1960, p. 403.

prepurified nitrogen. Oxygen and air used for the preparation of the oxygen adducts were dried ( $P_2O_5$ ). Solvents were carefully dried. Dimethylformamide, after being dried over molecular sieves, was distilled *in vacuo* to minimize decomposition to dimethylamine. Unless otherwise stated, all the oxygen adducts of Table 3 were prepared from filtered solutions of the cobalt-Schiff's base complex. The analyses of the combined molecular oxygen were carried out in the gas-volumetric equipment described previously.<sup>28</sup>

*NN'*-Ethylenebis(salicylideneiminato)cobalt(II).—This was prepared by a slight modification of the known procedure<sup>1,3</sup> from equimolar quantities of cobalt acetate and the Schiff's base in dimethylformamide. The red crystalline precipitate of the cobalt complex was filtered off, washed, and dried *in vacuo* at room temperature for about 5 hr. (82% yield). The product was recrystallised from dimethylformamide (Found: C, 59.2; H, 4.3; Co, 18.1; N, 8.8; Calc. for  $C_{38}H_{42}CoN_4O_8$ : C, 59.09; H, 4.34; Co, 18.12; N, 8.61%). The preparation in dimethyl sulphoxide gave similar results (Found: C, 59.0; H, 4.4; Co, 18.1; N, 8.7%).

*dimethylformamidocobalt(III)* (I).—A  $8.2 \times 10^{-3}M$  solution of Cosalen in dimethylformamide was slowly exposed to dry air without stirring. During 2 days the black crystalline precipitate was filtered off, washed with diethyl ether, and dried in a stream of air (40% yield). The oxygen adduct is a black crystalline solid insoluble in all common organic solvents, rapidly decomposed by halogenated solvents and benzene. The compound so obtained was used for the magnetic measurements (Table 1 and Figure 3). Less crystalline products of the same analytical composition were obtained by carrying out the oxygenation with pure oxygen or from suspensions of Co salen.

$\mu$ -Peroxo-bis-[*NN'*-ethylenebis(salicylideneiminato)(dimethyl sulphoxide)cobalt(III)] (II).—This was prepared by a procedure similar to that for the oxygen adduct (I) starting with an approximately  $1.3 \times 10^{-2}M$  solution of Co salen in dimethyl sulphoxide (70% yield).

$\mu$ -Peroxo-bis-[*NN'*-ethylenebis(salicylideneiminato)(pyridine oxide)cobalt(III)] (III).—This was obtained by treating with oxygen 10.2 mmoles of Co salen partially dissolved

TABLE 3  
Analytical data of oxygen adducts prepared from solution

Compound	Formula	Analysis (%)									
		C		H		Co		N		Other	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
(Co salen) <sub>2</sub> O <sub>2</sub> (DMF) <sub>2</sub> (I)	$C_{38}H_{42}Co_2N_4O_8$	55.25	55.08	5.08	5.11	14.29	14.22	10.11	10.14	3.85	3.86
(Co salen) <sub>2</sub> O <sub>2</sub> (DMSO) <sub>2</sub> (II)	$C_{38}H_{40}Co_2N_4O_8S_2$	51.35	51.55	4.68	4.81	14.55	14.05	6.77	6.68	3.75	3.81
(Co salen) <sub>2</sub> O <sub>2</sub> (pyO) <sub>2</sub> (III)	$C_{42}H_{38}Co_2N_6O_8$	57.84	57.81	4.54	4.39	13.50	13.51	9.81	9.63	3.41	3.67
(Co 3-methoxysalen) <sub>2</sub> O <sub>2</sub> (DMSO) (V)	$C_{38}H_{42}Co_2N_4O_{11}S$	52.02	51.82	4.88	4.81	13.76	13.38	6.65	6.36	3.49	3.64
(Co 5-chlorosalen) <sub>2</sub> O <sub>2</sub> (DMSO) <sub>2</sub> (VI)	$C_{38}H_{38}Cl_2Co_2N_4O_8S_2$	44.26	44.28	3.57	3.72	12.07	12.07	5.86	5.74	14.42	14.52
										6.34	6.57
Co 3-methoxysalen, py, O <sub>2</sub> (VII)	$C_{23}H_{28}CoN_2O_6$	55.54	55.65	4.78	4.67	11.70	11.87	8.47	8.47	—	—

The 3-methoxy- and the 5-chloro-derivatives of Co salen were prepared as described by Earnshaw *et al.*<sup>12</sup> The purity was checked by elemental analysis.

*NN'*-Ethylenebis-(3-methoxysalicylideneiminato)pyridinocobalt(II).—This was prepared from *NN'*-ethylenebis-(3-methoxysalicylideneiminato)cobalt(II) by dissolution in anhydrous pyridine and reprecipitation with heptane (Found: C, 59.3; H, 5.1; Co, 12.75; N, 9.2.  $C_{29}H_{23}CoN_3O_4$  requires C, 59.49; H, 4.99; Co, 12.69; N, 9.05%). The compound does not melt below 320°. Magnetic susceptibility measurements at 297°K:  $\chi_M^{corr} = 5788$  c.g.s.u.;  $\mu_{eff} = 3.70$  B.M. The diamagnetic correction was 257 c.g.s.u. per mole.

*NN'*-Iminodi-*n*-propylbis(salicylideneiminato)cobalt(II), Co salPr.—This was prepared according to a known procedure<sup>3</sup> from cobalt(II) acetate and the Schiff's base in water-ethyl alcohol. The monohydrate so obtained was then heated at 100–120° *in vacuo* for 2 hr. The product after recrystallisation from toluene was heated at 100° *in vacuo* for 14 hr. Shorter times of heating *in vacuo* result in products still containing solvent of recrystallisation. The final compound was a yellow brown microcrystalline powder which was inactive towards oxygen in the solid state, m.p. 246–248° (Found: C, 60.5; H, 6.1; Co, 14.85; N, 10.6. Calc. for  $C_{20}H_{28}CoN_3O_2$ : C, 60.61; H, 5.85; Co, 14.87; N, 10.60%).

$\mu$ -Peroxo-bis-[*NN'*-ethylenebis(salicylideneiminato)-

in dimethylacetamide (50 ml.) containing 24.2 mmoles of pyridine oxide (77% yield).

$\mu$ -Peroxo-bis-[*NN'*-ethylenebis(salicylideneiminato)pyridinocobalt(III)] (IV).—This was prepared according to the known procedure<sup>3</sup> and checked by elemental analysis [Found: C, 60.1; H, 4.5; Co, 14.0; N, 9.8; O<sub>2</sub>, 0.85 (with chloroform), 0.70 (with benzene).  $C_{42}H_{38}Co_2N_6O_8$  requires C, 60.01; H, 4.56; Co, 14.02; N, 10.00; O<sub>2</sub>, 3.81%].

Oxygen Adducts of Cobalt 3-Methoxy and 5-Chloro-salen (V) and (VI).—These were obtained by procedures substantially identical to that described above for compound (III).

$\mu$ -Peroxo-bis-[*NN'*-ethylenebis(salicylideneiminato)cobalt(III)].—This was prepared as described previously<sup>8</sup> from Co salen,  $CHCl_3$  followed by removal of chloroform *in vacuo* at 100° for 1 hr. The active Co salen so obtained was exposed to dry oxygen for 20 hr. with vigorous stirring. The oxygen adduct is a black microcrystalline solid, rapidly decomposed to the starting cobalt complex by chloroform and benzene or by heating (Found: C, 56.5; H, 4.2; Co, 17.15; N, 8.03; O<sub>2</sub>, 4.6. Calc. for  $C_{32}H_{28}Co_2N_4O_8$ : C, 56.32; H, 4.14; Co, 17.27; N, 8.21; O<sub>2</sub>, 4.69%);  $\chi_M$  (c.g.s.u.) at the temperatures indicated (average of four determinations at different magnetic fields between 9600 and 11,000 oersted): 239 (296°K); 290 (240°K); 316 (210°K); 356 (180°K); 408 (150°K); 563 (90°K). The Curie-Weiss law is followed with  $\theta$  ca. +60°.

<sup>28</sup> F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, 1, 30.

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*NN'*-*Iminodi-n-propylbis(salicylideneiminato)cobalt(II)* (1.17 g.) was dissolved in 15 ml. of tetrahydrofuran under nitrogen and the resulting red-brown solution was exposed to dry oxygen for *ca.* 12 hr. with vigorous stirring. The brown precipitate formed during this time was kept under oxygen for a few hours without stirring and then filtered off and dried in a stream of dry oxygen (39% yield). The product analysed correctly for  $\text{Co salPr}_2\text{O}_2$  (Found: C, 55.65; H, 5.5; Co, 13.7; N, 9.6.  $\text{C}_{20}\text{H}_{23}\text{CoN}_3\text{O}_4$  requires C, 56.08; H, 5.41; Co, 13.76; N, 9.81%).

*Oxygen-NN'-ethylenebis-(3-methoxysalicylideneiminato)-pyridinocobalt(II)* (VII).—This was prepared by dissolving 2.06 g. of *NN'*-ethylenebis-(3-methoxysalicylideneiminato)-cobalt(II) in 200 ml. of anhydrous pyridine under nitrogen and then exposing this solution to dry oxygen for 24 hr. The brown-red precipitate formed during this time was filtered off, washed with heptane, and dried in a stream of dry air (77% yield).

*Effect of Ligand Environment on the Oxygenation of the Cobalt Complexes.*—The formation of the 1:2 oxygen adducts of Co salen and its ring-substituted analogues and of the 1:1 adducts was investigated by gas-volumetric measurements of the oxygen absorbed (Table 2). The samples of the cobalt complexes were contained in thin-walled vials to be broken by a magnetic stirrer at the given moment. The oxygenation was initially fast. The re-

action conditions were maintained for several hours till the volume was constant. When 1:2 adducts were formed, the gas absorption was generally complete within about 2 hr.

*Decomposition of the Oxygen Adducts.*—Compounds (I), (II), (III), and  $(\text{Co salen})_2\text{O}_2$  evolved quantitatively the combined molecular oxygen by treatment with chloroform or benzene at room temperature. The initial Co salen and the ligand co-ordinated to cobalt in the oxygen adduct were recovered from the reactions with chloroform and recognised by elemental analysis and i.r. spectroscopy, respectively. In the case of the other compounds, the reaction with chloroform gave partial [compounds (V) and  $(\text{Co salen})_2\text{O}_2\text{py}_2$ ] or no evolution [compound (VI)] of oxygen. Also no oxygen evolution was observed from Co 3-methoxysalen,  $\text{py}_2\text{O}_2$  upon treatment with chloroform and benzene. Thermal decompositions *in vacuo* at *ca.* 100° were then carried out. The residue resulting from the elimination of the volatile products was recrystallised from chloroform and recognised as the starting cobalt(II) complex by elemental analysis. In the case of  $\text{Co salPr}_2\text{O}_2$  heating *in vacuo* at 100° did not result in an apparent change.

We thank Dr. J.-J. Salzmann for some magnetic susceptibility measurements.

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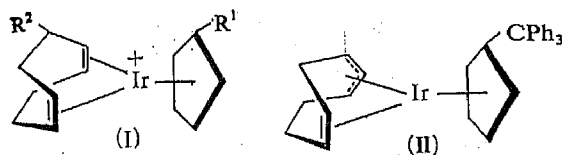
## The Chemistry of Co-ordinated Ligands. Part III.† The Reaction of the Triphenylmethyl Cation with some Transition-metal Complexes of Cyclo-octa-1,5-diene, Dicyclopentadiene, and Norbornadiene

By J. Lewis \*† and A. W. Parkins, Department of Chemistry, The University, Manchester 13

Cyclopentadienyl(cyclo-octa-1,5-diene)iridium reacts with 1 and 2 mol. of triphenylmethyl fluoroborate to give  $\text{Ph}_3\text{C}\cdot\text{C}_8\text{H}_4\text{IrC}_8\text{H}_{12}$  and  $\text{Ph}_3\text{C}\cdot\text{C}_8\text{H}_4\text{IrC}_8\text{H}_{11}^+$  respectively. The cation  $\text{C}_8\text{H}_5\text{CoC}_{10}\text{H}_{11}^+$  derived from dicyclopentadiene, has been synthesised and its n.m.r. spectrum assigned. The reaction between cyclopentadienyl(norbornadiene)-cobalt and triphenylmethyl fluoroborate in dichloromethane is complex. The cation  $\text{C}_8\text{H}_5\text{CoC}_7\text{H}_8^+$  has been obtained from the aqueous extract of the reaction mixture and the overall stoichiometric result is protonation. The three cations add nucleophiles to give neutral derivatives.

*Cyclo-octa-1,5-diene Complexes.*—Hydride-ion abstraction by the triphenylmethyl (trityl) cation from co-ordinated cyclo-octa-1,5-diene in cyclopentadienyl(cyclo-octa-1,5-diene)cobalt and the rhodium analogue leads<sup>1</sup> to the cyclo-octa-2,5-dienyl ligand which contains an unconjugated olefinic bond and a  $\pi$ -allyl system within the eight-membered ring. With the rhodium compound electrophilic substitution of the cyclopentadienyl ring occurs before hydride-ion abstraction. Cyclopentadienyl(cyclo-octa-1,5-diene)iridium reacts in the same way on treatment with trityl fluoroborate. With 1 mol. of the reagent the neutral compound tritylcyclopentadienyl(cyclo-octa-1,5-diene)iridium (I;  $\text{R}^1 = \text{Ph}_3\text{C}$ ,  $\text{R}^2 = \text{H}$ ) is obtained the n.m.r. spectrum of which ( $\text{DCCl}_3$ ) shows peaks at  $\tau$  2.7 (15H), 4.8 (2H), 5.3 (2H), 6.6 (4H),

and 8.2 (SH). The resonance at 2.7 is due to the phenyl protons and those at 6.6 and 8.2 are due, respectively, to the co-ordinated olefinic and saturated protons of the cyclo-octa-1,5-diene ligand. These are at slightly higher field than the corresponding resonances at  $\tau$  6.2 and 8.1 in the unsubstituted complex,<sup>2</sup> but have very similar line-shapes. The cyclopentadienyl resonances at  $\tau$  4.8



and 5.3 appear as triplets owing to coupling in the cyclopentadienyl ring.

As in the rhodium series a cationic cyclo-octa-2,5-dienyl complex can be obtained by using 2 mol. of

<sup>1</sup> J. Lewis and A. W. Parkins, *J. Chem. Soc. (A)*, 1967, 1150.

<sup>2</sup> S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.

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† Part II, A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

Other	and Calc.
	O <sub>2</sub>
35	3.86
75	3.81
41	3.67
	S
49	3.64
	Cl
42	14.52
	S
44	0.57