Synthesis and Characterisation of Some Cobalt(II) Complexes of Schiff-base Ligands and Their Reactions with Molecular Oxygen. Effects of Chelate Ring Size†

Fathy M. Ashmawy, Rafat M. Issa,* and Saiid A. Amer
Department of Chemistry, University of Tanta, Tanta, Egypt
Charles A. McAuliffe* and R. V. ('Dick') Parish
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

A series of potentially tetradentate Schiff-base ligands, for example N,N'-ethylenebis(1-hydroxy-2-naphthylmethyleneimine) (H_2napen), in which the methylene linkage between the imine donors varies from C_2 to C_6, have been complexed to cobalt(II). Two types of complex are formed: $CoL(H_2O)_n$ ($n = 0$, complex is planar; $n = 2$, complex is pseudo-octahedral) in which the ligand binds as a dianionic tetradentate N_2O_2 donor, and $Co(H_2L)Cl_2$, which are pseudo-tetrahedral and the ligand is neutral, binding through the imine groups only. The structure seems to be mainly dependent on the length of the methylene chain of the ligand. The reversible reaction of [Co(napen)] with dioxygen in N,N-dimethylformamide has been studied at a number of temperatures and thermodynamic data and binding curves obtained; the enthalpy of reaction ($\Delta H^\circ = -78.8$ kJ mol^{-1}) is significantly different from that of the well studied [Co(salen)] [H_2salen = N,N'-ethylenebis(salicylideneimine)] in dimethyl sulphoxide ($\Delta H^\circ = -66.9$ kJ mol^{-1}). The reaction of the other complexes with dioxygen crucially depends upon the complex geometry and its physical state (solution or slurry). Irreversible oxidation of cobalt(II) to cobalt(III) is observed for a number of complexes.

Complexes of cobalt(II) involving derivatives of salicylaldehyde and aliphatic amines have received considerable attention because of their similarity to biological dioxygen carriers,[1-9] as well as their potential as catalysts for the insertion of oxygen into organic substrates.[10-12] In particular, the dioxygen adduct of N,N'-ethylenebis(salicylideneiminato)cobalt(II), [Co(salen)], (and its ring-substituted analogues) of formulae [Co(salen)-(O_2)L] and [{Co(salen)L}$_2$(O_2)] [L = pyridine, N,N-dimethylformamide (dmf), or dimethyl sulphoxide (dmso)] have received intensive investigation and have been reviewed recently.[13-15] Only limited studies have been made on [Co(napen)] [H_2napen = N,N'-ethylenebis(1-hydroxy-2-naphthylmethyleneimine)] and its dioxygen adduct. Although the complex [Co(napen)(O_2)(dmf)] exhibited an e.s.r. spectrum characteristic of a monomeric dioxygen adduct,[16,17] no thermodynamic data have been reported.

Here we describe the synthesis and characterisation of cobalt(II) complexes of a series of ligands of type (I). Two types of complex have been isolated, *viz.* those in which the ligand binds as a dianionic N_2O_2 donor system, and those in which the ligand acts as a neutral N_2 donor binding *via* the imine groups. We have examined the reaction of dioxygen with these complexes and have observed some significant differences between these and, for example, the [Co(salen)] system.

Results and Discussion

Two types of complex were isolated: the $CoL \cdot nH_2O$ complexes (1)—(4), containing dianionic ligands, were synthesised by reaction of L^{2-} with cobalt(II) acetate in ethanol, and the $Co(H_2L)Cl_2 \cdot nH_2O$, complexes (5)—(8), containing neutral ligands, were synthesised by the reaction of H_2L with cobalt(II) chloride in ethanol (see Experimental section). The complexes are listed in Table 1, together with their analytical data; in some cases molecules of water form part of the co-ordination sphere.

(I)

R
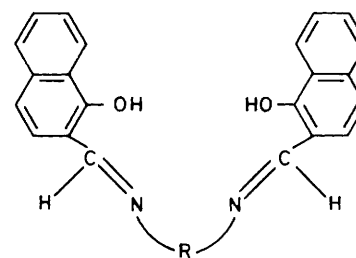
	R
H_2napen	$(CH_2)_2$
H_2nappn	$(CH_2)_3$
H_2napbu	$(CH_2)_4$
H_2nappen	$(CH_2)_5$
H_2naphex	$(CH_2)_6$

Infrared Spectra.—The i.r. spectra, Table 2, show bands typical of Schiff-base complexes, with strong peaks in the 1 650—1 500 cm^{-1} region.[18-20] There were generally three peaks in this region which could be assigned to ν(CN) and ν(C=C) vibrations, with shoulders observed on these peaks in a number of cases. The ν(CN) band is of particular interest since its energy is diagnostic of the mode of co-ordination of the ligands: when co-ordinated as the dianionic tetradentate N_2O_2 species the ν(CN) band is shifted to lower energy by 15—35 cm^{-1} from that in the free ligand, see Table 2, complexes (1)—(4),[21] whilst co-ordination as a neutral bidentate ligand *via* the azomethine nitrogens, complexes (5)—(8), shifts this band to higher frequencies, the magnitude of this shift being only of the

Table 1. Some analytical data and physical properties of the complexes

Complex	Colour	$\mu_{eff.}$/B.M.	g	Analysis * (%)				
				C	H	N	Co	Cl
(1) [Co(napen)]	Red	2.7	2.355	68.3 (68.1)	4.0 (4.3)	6.6 (6.6)	13.7 (13.9)	
(2) [Co(nappn)(H₂O)₂]	Olive	5.3	$g_{\parallel}$ = 1.974, $g_{\perp}$ = 1.982	64.1 (63.2)	4.7 (5.1)	5.4 (5.9)	12.7 (12.4)	
(3) [Co(napbu)(H₂O)₂]·H₂O	Olive	4.4	$g_{\parallel}$ = 1.974, $g_{\perp}$ = 1.982	62.2 (61.5)	5.1 (5.1)	5.1 (5.5)	10.8 (11.6)	
(4) [Co(naphex)(H₂O)₂]	Orange	4.5	2.768	65.9 (65.1)	5.2 (5.1)	5.3 (5.4)	11.8 (11.4)	
(5) [Co(H₂napen)Cl₂(H₂O)₂]·H₂O	Brown	4.9		51.7 (52.4)	4.3 (4.7)	5.7 (5.1)	11.2 (10.7)	12.6 (12.9)
(6) [Co(H₂napbu)Cl₂]·2H₂O	Green	4.4	2.983	55.2 (55.5)	4.5 (5.0)	4.7 (5.0)	9.5 (10.5)	12.0 (12.6)
(7) [Co(H₂nappen)Cl₂]	Green	4.4		59.0 (59.2)	5.5 (4.9)	5.3 (4.2)	10.2 (10.9)	13.1 (13.1)
(8) [Co(H₂naphex)Cl₂]	Green	4.3		59.5 (60.6)	5.6 (5.1)	4.8 (5.1)	9.9 (10.6)	12.5 (12.8)

* Calculated values in parentheses.

Table 2. Significant infrared bands (cm⁻¹) for the complexes[a]

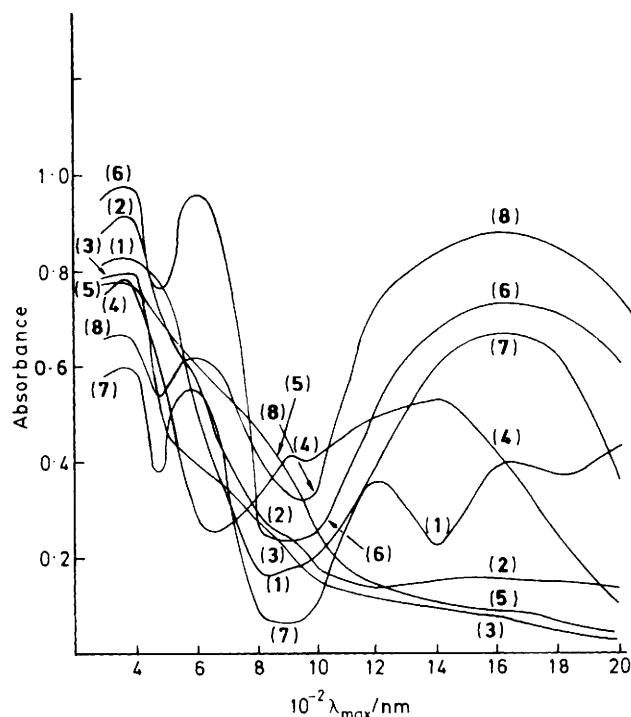| Complex	ν(C=N)[b]	ν(Co–O)	ν(Co–N)	ν(Co–Cl)
(1)	1 600 (1 625)	435	365	
(2)	1 610 (1 625)	435	385	
(3)	1 615 (1 630)	418	385	
(4)	1 600 (1 635)	422	382	
(5)	1 630 (1 625)		362	320, 285
(6)	1 640 (1 630)		365	330, 300
(7)	1 640 (1 635)		370	325, 295
(8)	1 640 (1 635)		372	336, 288

[a] Nujol mulls. [b] Free ligand values in parentheses.

Table 3. Electronic spectra of the complexes in solution

	$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm³ mol⁻¹ cm⁻¹)	
Complex	dmf	Chloroform
(1)	360 (17 100), 380 (17 000), 424 (18 300), 448 (13 000), 500 (4 300), 540 (1 300)	360 (18 000), 380 (18 000), 428 (20 000), 455 (14 000), 515 (4 700), 545 (2 100)
(2)	400 (7 800), 420 (7 900), 460 (2 900)	400 (4 100), 420 (4 200), 460 (1 500)
(3)	360 (6 200), 400 (1 200), 420 (1 300)	360 (1 200), 400 (19 800), 420 (20 000)
(4)*	360, 400, 420	360, 400, 420
(5)*	380, 400, 422	600, 670
(6)	360 (8 500), 380 (9 400), 400 (10 700), 420 (9 400)	600 (200), 670 (250)
(7)	360 (8 200), 380 (11 000), 400 (14 000), 420 (11 200)	600 (170), 670 (300)
(8)	360 (7 500), 400 (18 500), 420 (19 500)	600 (200), 670 (300)

* Saturated solutions.
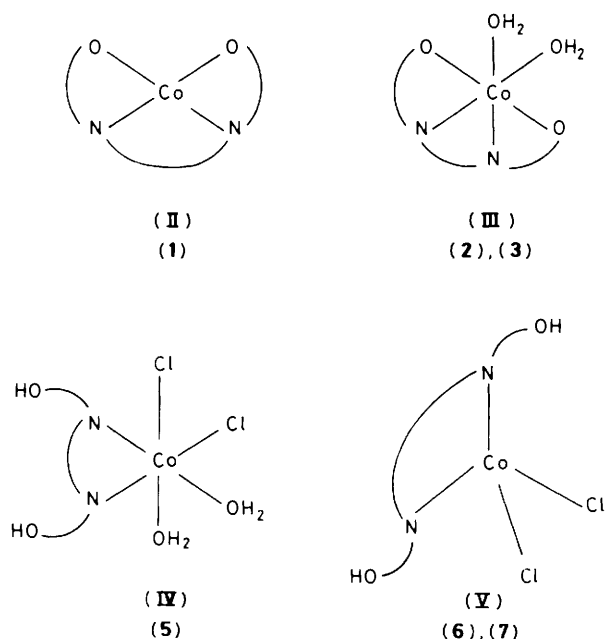

Figure 1. Reflectance spectra of the complexes

order of 5—10 cm⁻¹.[22–24] Where analytical data suggest the presence of water molecules broad absorptions are present centred at *ca.* 3 450 cm⁻¹. Other significant bands are listed in Table 2.

Electronic Spectra.—Solution electronic spectral data are listed in Table 3, whilst the reflectance spectra are illustrated in Figure 1. On the basis of their reflectance spectra the complexes can be classified into three categories: (A) [complex (1)], (B) [complexes (2), (3), (5)], and (C) [complexes (4), (6)—(8)]. The spectrum of complex (1) exhibits a band at 1 200 nm, which is characteristic of square-planar cobalt(II) species.[25] Complexes of type (B) show absorption bands at 880—800 and 600—500 nm, and these spectra do not agree either in band position or in general appearance with the spectra of known pseudo-tetrahedral bis(salicylideneiminato)cobalt(II) complexes.[26]

However, the band at 880—800 nm may be assigned to the low symmetry components of the octahedral $^4T_{1g}(F)$ ⟶ $^4T_{2g}(F)$ transition. The remaining bands at 600—500 nm are too close in energy to the charge-transfer bands to be assigned with any degree of confidence. The spectra of the type (C) complexes show absorption bands at 1 400—1 200, 600—500, and 400 nm. The first band can be assigned to low symmetry components of the second tetrahedral transition $^4A_2$ ⟶ $^4T_1(F)$, while the band at 600—500 nm is assigned to the $^4A_2$ ⟶ $^4T_1(P)$ transition.

Magnetic and E.S.R. Data.—Room-temperature magnetic moments, Table 1, are consistent with the structures assigned to the complexes from their electronic spectra, *viz.* that complex (1) is planar, $\mu_{eff.}$ = 2.7 B.M.; that the other complexes are pseudo-tetrahedral or pseudo-octahedral, $\mu_{eff.}$ = 4.3—5.3 B.M. With the exception of complexes (2) and (3) the compounds give strong, broad e.s.r. signals centred at *ca.* g = 2.45. On the other hand complexes (2) and (3) exhibit e.s.r. signals containing hyperfine splitting with g values of $g_{\perp}$ = 1.982 and $g_{\parallel}$ = 1.974
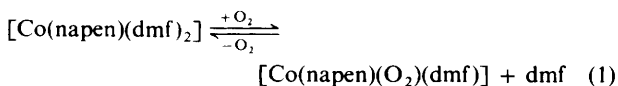
(II)
(1)

(III)
(2),(3)

(IV)
(5)

(V)
(6),(7)

Figure 2. Variation of the electronic spectrum of [Co(napen)] (1) in dmf with dioxygen partial pressure at $-30\ ^\circ C$: $p(O_2) = 0\ (i)$, 40 (ii), 80 (iii), 150 (iv), 200 (v), 400 (vi), and 640 Torr (vii)

Figure 3. Solution isotherms for [Co(napen)] (1) in dmf at -10 (○), -30 (△), and $-50\ ^\circ C$ (□)

characteristic of cobalt(II) complexes in an axially distorted octahedral configuration.[27]

Structures.—Based on spectral and magnetic data we propose the structures of the type illustrated, (II)—(V). Although crystal structures are not available, the proposed structures are consistent with all other evidence. It can be seen that quite small changes in ligand structure result in quite dramatic differences in metal complex structure. For example napen forms a planar complex, whilst nappn produces a pseudo-octahedral complex; molecular models indicate that there are severe steric strains in attempts to fit nappn in a planar configuration. Of course, this multiplicity of structures obtained is not surprising, since there is a lack of crystal-field stabilisation for any particular cobalt(II) geometry.

Reaction with Dioxygen.—The passage of dioxygen through the red solution of (1) in dry dmf at low temperatures, $<0\ ^\circ C$, causes a rapid colour change to brown. The red colour of the original complex can be restored either by lowering the pressure above the oxygenated solution or by warming to room temperature. However, addition of dioxygen at room temperature causes a slow irreversible decomposition of (1).

We have measured the amount of O_2 absorbed by (1) in dmf. We observe that *ca.* 80% of the O_2 absorbed is taken up quickly, typically in 6—8 min under the conditions employed, but further absorption is very slow. In a typical experiment at $-10\ ^\circ C$ the O_2 uptake by the complex (*i.e.* discounting solvent uptake) was found to be 3.20×10^{-3} mol per 3.40×10^{-3} mol of (1), which is indicative of a 1:1 [Co(napen)(O_2)(dmf)] complex in solution. The reverse of reaction (1), brought about by warming the solution under

$$[Co(napen)(dmf)_2] \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}}$$

$$[Co(napen)(O_2)(dmf)] + dmf \quad (1)$$

vacuum, is complete in a matter of minutes. The process was found to be *ca.* 98% reproducible after three cycles at $p(O_2) = 560$ Torr.
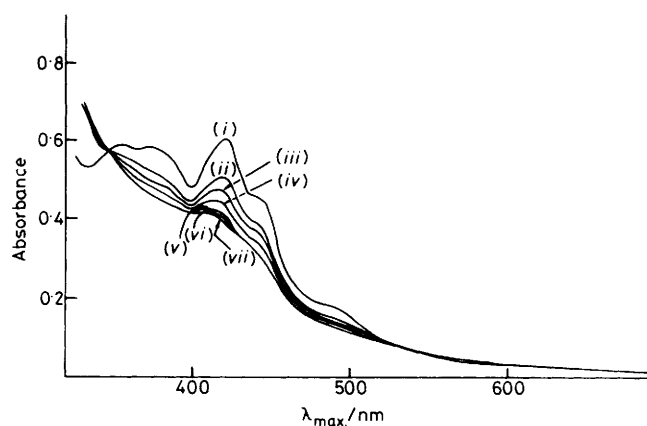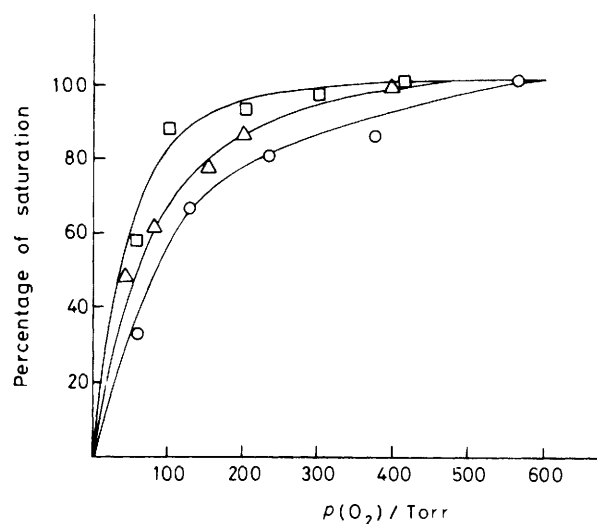
The electronic spectrum of (1) in dmf is characterised by

absorption maxima at 500, 448, 424, 380, and 360 nm. Spectral changes during dioxygenation were recorded at different dioxygen partial pressures and in the temperature range -10 to $-50\ ^\circ C$ (see Experimental section). Upon dioxygenation the bands at 380 and 360 nm diminish in intensity and eventually disappear, while the band at 424 nm broadens and its intensity falls. The spectra exhibit two isosbestic points at 540 and 350 nm, Figure 2. Subsequently the original spectrum of (1) can be regenerated by flushing the sample with argon.

Dioxygen Binding Curves.—The formation of [Co(napen)-(O_2)(dmf)] in solution is a function of $p(O_2)$ and this may be followed spectrophotometrically. The percentage saturation of the [Co(napen)(dmf)$_2$] was calculated from the ratio of the absorption intensity of the 424 nm band (Figure 2) at any $p(O_2)$ relative to that at 100% saturation, which was in turn judged by the constancy of the spectrum upon further increase in $p(O_2)$; typically, this equilibrium was reached in 40—60 s. Isotherms constructed for the reaction of [Co(napen)] in dmf with dioxygen in the temperature range -10 to 50 $^\circ C$ in this way are shown in Figure 3.

Table 4. Thermodynamic data for the reaction [Co(napen)(dmf)$_2$] + $O_2 \xrightarrow{K_{O_2}}$ [Co(napen)(O$_2$)(dmf)] + dmf

Temp./ °C	log (K_{O_2}/ Torr^{-1})	K_{O_2}/ Torr^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}	ΔG°/ kJ mol^{-1}
−10	−2.48	3.3			
−30	−2.04	9.1	−78.80	−221.90	−13.80
−50	−1.80	15.8			

Figure 5. E.s.r. spectra of the dioxygen complex of [Co(napen)] (1) in dmf at liquid nitrogen temperature

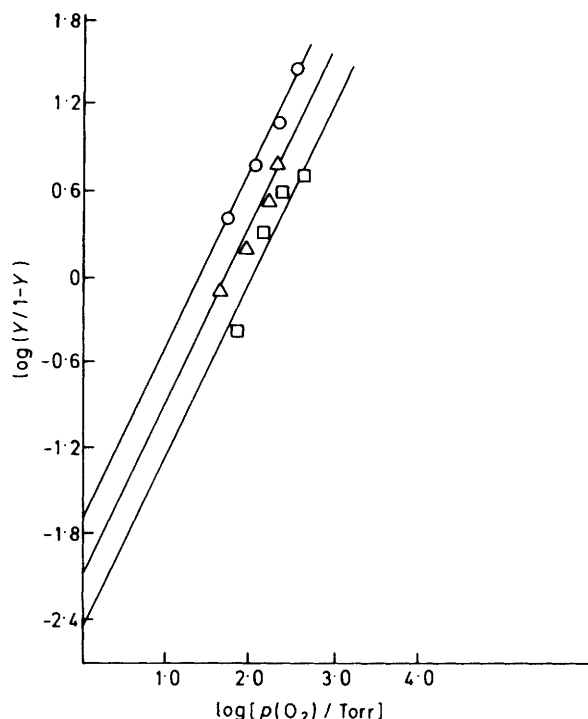**Figure 4.** Hill plot for [Co(napen)] (1) in dmf at −10 (□), −30 (△), and −50 °C (○)

The equilibrium constant for reaction (1), K_{O_2}, was calculated from the isotherms using the Hill equation [equation (2)],

$$K_{O_2} = \frac{[\text{Co(napen)(O}_2)(\text{dmf)}]}{[\text{Co(napen)(dmf)}_2] \cdot p(\text{O}_2)^n} = \frac{Y}{1-Y} \quad (2)$$

where Y is the fraction of the dioxygenated sites and $p(\text{O}_2)$ is the partial pressure. A plot of log ($Y/1 - Y$) versus log $p(\text{O}_2)$ is the Hill plot, and yields lines of slope n (the Hill coefficient), which are nearly equal to 1 (Figure 4). These values indicate that there is no co-operativity in the binding of dioxygen to complex (1) in dmf. The values of log K_{O_2} at the different temperatures are obtained from the intercepts of the best straight lines. Other thermodynamic data are also listed in Table 4. The enthalpy of the reaction of (1) with dioxygen in dmf ($\Delta H^\circ = −78.8$ kJ mol^{-1}) shows that (1) forms a more stable dioxygen adduct than does [Co(salen)] in dmso ($\Delta H^\circ = −66.9$ kJ mol^{-1}).[28]

The e.s.r. spectrum of the adduct, Figure 5, was obtained in dmf solution by the use of X-band at liquid nitrogen temperature. Two signals, $g_{\parallel} = 2.093$ and $g_{\perp} = 1.996$, with hyperfine splitting, are characteristic of monomeric dioxygenated cobalt complexes.[7,8,14] The adduct can best be described as a cobalt(III) species co-ordinated to superoxide.[4,15] The hyperfine splitting indicates axial symmetry, which probably
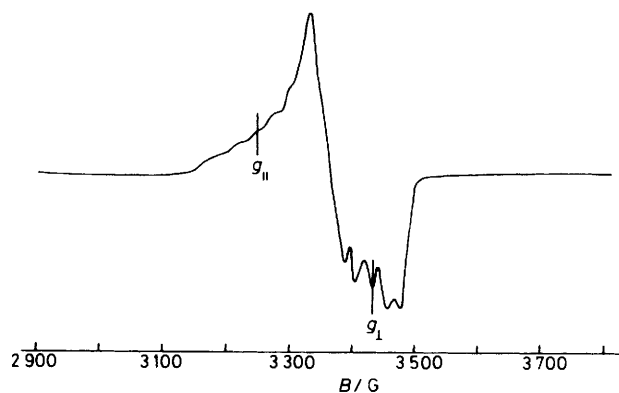
arises from strongly bound dmf.[16,17] Attempts were made to dioxygenate complex (1) as a slurry in dmf. No reaction was observed.

Reaction of Complexes (2)—(8) *with Dioxygen.*—The reaction of (2) and (3) (the complexes assigned pseudo-octahedral structures) in dmf solution with dioxygen at room temperature or below (to −50 °C) produced no change in their visible spectra, strongly suggesting that these complexes do not react with dioxygen in dmf. However, as slurries in chloroform both complexes (2) and (3) appear to change colour as they are exposed to dioxygen to a somewhat more vivid green. The analyses of these complexes closely correspond to [CoL(OH)] (L = dianion of Schiff-base ligand) and their diamagnetism strongly suggests that (2) and (3) are oxidised to cobalt(III) on exposure to dioxygen in chloroform. Their visible spectra exhibit a strong band at 600 nm which is absent in the spectra of (2) and (3). The i.r. spectra of the cobalt(III) complexes are very similar to those of (2) and (3), indicating that oxidation has occurred at the metal and not at the co-ordinated ligand.

Complex (4) and the complexes containing the neutral ligand, (5)—(8), do not appear to react with dioxygen either in dmf solution or as slurries in dmf or chloroform.

Conclusions

We have shown that the type of complex formed between cobalt(II) acetate tetrahydrate and the potentially tetradentate N$_2$O$_2$ Schiff-base ligands is determined by the length of the carbon chain linking the imine groups, further, that the subsequent reaction with dioxygen crucially depends upon the structure of the cobalt(II) complex and upon its physical state (solution in dmf or as a slurry). Both reversible binding of dioxygen and irreversible oxidation of the metal have been observed. Complexes containing the neutral ligand co-ordinated as an N$_2$ donor, [Co(H$_2$L)Cl$_2$], show no reaction with dioxygen under the conditions employed.

Experimental

The ligands were prepared by standard methods.

Complex Preparations.—*Complexes* (1)—(4). The ligand (0.05 mol) dissolved in dioxygen-free hot ethanol (50 cm^3) was mixed with trimethylamine (0.1 mol) and this was then added with stirring to cobalt(II) acetate tetrahydrate (0.05 mol) in dioxygen-free ethanol (50 cm^3), resulting in the immediate precipitation of the complex. The complex was filtered off,
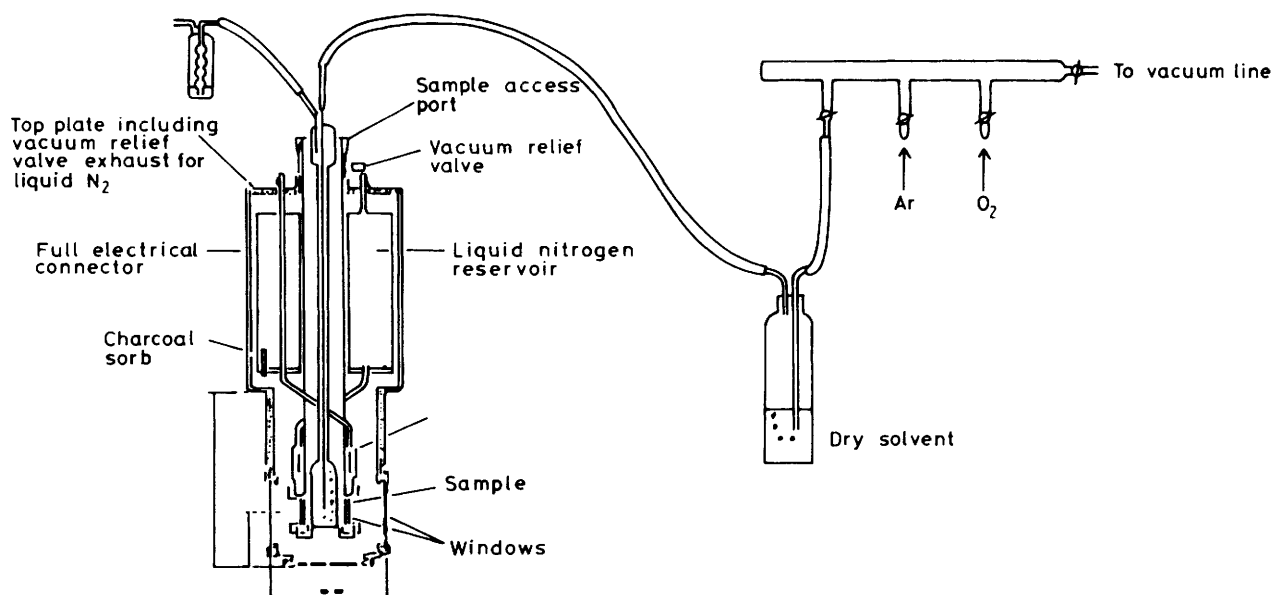
Figure 6. Apparatus used for the electronic spectral measurements at low temperatures

washed with acetone (3 × 20 cm³), and dried *in vacuo*. The complexes were stored and handled under dry dinitrogen. Yields *ca.* 95%.

Complexes (5)—(8). The ligand (0.1 mol) dissolved in ethanol (100 cm³) was mixed with cobalt(II) chloride hexahydrate (0.1 mol) in ethanol (25 cm³). The mixture was stirred and heated to reflux for 30 min, cooled and the resulting precipitate filtered off, washed with ethanol (3 × 20 cm³) and diethyl ether (3 × 20 cm³), and dried *in vacuo*. Yields are quantitative. The complexes are air stable.

Except for (1) the complexes (1)—(4) have limited solubility in dmf and chloroform. Complexes (5)—(8) are somewhat soluble in dmf, and all the complexes are insoluble in acetone, ethanol, and methanol.

Physical Measurements.—These were obtained as previously described.[21]

Measurement of Dioxygen Uptake.—The apparatus and method employed has been fully described elsewhere (essentially a gas burette, gas reservoir, and uptake flask immersed in a constant temperature bath).[29] Dioxygen uptake by solvent blanks was also determined.

Solution Isotherm Measurement at Low Temperature.—The apparatus used is shown in Figure 6. A DN 1704 variable-temperature liquid nitrogen cryostat was connected to a vacuum line. A special cell with a long neck, fitted with a ground-glass tap, was loaded with the deoxygenated solution of the complex under dry argon. It was transferred to the variable-temperature device and allowed to reach the desired temperature. Once thermal equilibrium had been reached the cell was connected to the vacuum line, the pressure being measured with a line manometer, and the pressure made up to atmospheric with dry argon. The gas mixture (O_2–Ar) was then introduced into the cell and the spectrum followed with time until no further change was observed, indicating that equilibrium had been reached between dioxygenated and unoxygenated species. The procedure was repeated for a new solution and a new O_2–Ar mixture. Complete (100%) saturation was judged by the constancy of the spectrum upon further increase in $p(O_2)$.

References

1 C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 1969, 946.
2 S. Yamada, *Coord. Chem. Rev.*, 1966, 1, 415.
3 L. S. Chen, M. E. Koehler, B. C. Bestel, and S. C. Cummings, *J. Am. Chem. Soc.*, 1978, 100, 7243.
4 R. L. Lancashire, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1979, 66.
5 W. Kanda, H. Okawa, and S. Kida, *J. Chem. Soc., Chem. Commun.*, 1983, 973.
6 R. Machida, E. Kimura, and H. Kodama, *Inorg. Chem.*, 1983, 22, 2055.
7 R. Kasuga, T. Nagahara, A. Tsuge, K. Sogabe, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, 56, 95.
8 B. J. Trzebiatowska, P. Chmielewski, and A. Vogt, *Inorg. Chim. Acta*, 1984, 83, 129.
9 R. J. Motekaitis, A. E. Martell, and D. A. Nelson, *Inorg. Chem.*, 1984, 23, 275.
10 D. L. Tomaja, L. H. Vogt, and J. G. Wirth, *J. Org. Chem.*, 1970, 35, 2029.
11 A. Nishinaga, T. Tojo, and T. Matsuura, *J. Chem. Soc., Chem. Commun.*, 1974, 896.
12 A. Nishinaga, H. Tomita, K. Nishizawa, and T. Matsuura, *J. Chem. Soc., Dalton Trans.*, 1981, 1504.
13 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, 79, 139.
14 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, 1981, 39, 295.
15 E. C. Niederhoffer, J. H. Timmons, and R. E. Martell, *Chem. Rev.*, 1984, 84, 137.
16 E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nucl. Chem. Lett.*, 1971, 7, 901.
17 E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nucl. Chem. Lett.*, 1973, 9, 151.
18 L. J. Boucher and M. O. Farrel, *J. Inorg. Nucl. Chem.*, 1973, 35, 3731.
19 L. J. Boucher, *Inorg. Chem.*, 1976, 15, 1334.
20 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish, and J. Tames, *J. Chem. Soc., Dalton Trans.*, 1985, 1391.
21 J. R. Dilworth, C. A. McAuliffe, and B. J. Sayle, *J. Chem. Soc., Dalton Trans.*, 1977, 849.

22 A. V. Kogan, O. A. Dipov, V. I. Minkin, and V. P. Sodolov, *Russ. J. Inorg. Chem.*, 1965, **10**, 45.
23 C. A. McAuliffe, F. P. McCullough, M. J. Parrott, C. Arlyn Rice, B. J. Sayle, and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1977, 1762.
24 F. L. Bowden and D. Ferguson, *J. Chem. Soc., Dalton Trans.*, 1974, 460.
25 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1964, **8**, 37.
26 M. Hariharam and F. Urbach, *Inorg. Chem.*, 1969, **8**, 556.

27 A. Von Telewsky and H. Fievz, *Adv. Chim. Acta*, 1973, **56**, 977.
28 E. I. Ochiai, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1727.
29 C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie, and K. Minten, *J. Chem. Soc., Dalton Trans.*, 1983, 2147.