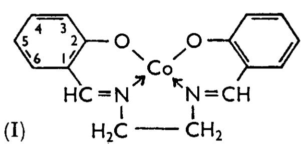
877. *Transition Metal–Schiff's Base Complexes. Part II.*[1] *The Reaction of Nitric Oxide with Some Oxygen-carrying Cobalt Compounds* *

By A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy

NN'-Ethylenebis(salicylideneiminato)cobalt(II) absorbs irreversibly one nitric oxide molecule per cobalt atom to give an apparently five-co-ordinate species; many substituted forms of this compound react similarly. Variations in the nitric oxide stretching frequencies in this series of mononitrosyls have been related to varying double-bond character in the cobalt–nitric oxide bond arising from the electron-repelling or attracting character of the substituents. With appropriate and suitably positioned substituents, it appears that a conjugated system can extend from the substituent to the nitric oxide molecule *via* the metal.

The quadridentate Schiff's base obtained by the condensation of salicylaldehyde with ethylenediamine will complex with many metals,[2-5] and the cobalt complex (I), *NN'*-ethylenebis(salicylideneiminato)cobalt(II), is particularly interesting, because it will combine reversibly with oxygen.[3] Diehl reported that the solid will absorb nitric oxide,[6] but he did not investigate the product. Preliminary work showed that this reaction did not give pure product, although approximately one mole of nitric oxide was absorbed per mole of the complex; but, in chloroform, a crystalline compound was formed, the analysis of which corresponded well with that of a mononitrosyl. However, even with a solvent present, direct reaction of the 3-methoxy- and 5-nitro-substituted cobalt complexes did not give pure mononitrosyls. All the compounds listed in Table 1, except the unsubstituted, were prepared under nitric oxide by mixing dimethylformamide solutions of cobalt acetate and the appropriate Schiff's base. This had the advantage over direct reaction that previous isolation of the cobalt–Schiff's base complexes was unnecessary.



(I)

Unlike its reaction with oxygen, the reaction of the complex (I), in solution or as the solid, with nitric oxide was irreversible. During a kinetic study, Rallo and Silvestroni[7] have recently found, that the solid absorbs irreversibly an equimolar quantity of nitric oxide.

These compounds are non-conducting in nitrobenzene and dimethylformamide. They are poorly soluble in most solvents, but the unsubstituted and 5,5'-dichloro-compounds

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* Previously published briefly in A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, 1963, **199**, 483.

[1] Part I, P. C. Hewlett and L. F. Larkworthy, *J.*, 1965, 882.

[2] P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Annalen*, 1933, **503**, 84.

[3] A. E. Martell and M. Calvin, " Chemistry of the Metal Chelate Compounds," Prentice Hall, New York, 1952, ch. 8.

[4] I. A. Savich, A. K. Pikaev, V. G. Lebedev, E. U. Kuz'micheva, and V. I. Spitsyn, *Russ. J. Inorg. Chem.*, 1962, **3**, 254.

[5] B. O. West, *Rev. Pure Appl. Chem.* (*Australia*), 1960, **10**, 207.

[6] H. Diehl, C. C. Hach, G. C. Harrison, L. M. Liggett, and T. S. Chao, *Iowa State Coll. J. Sci.*, 1947, **21**, 287.

[7] F. Rallo and P. Silvestroni, *Ricerca Sci.*, 1963, **3**, 1001.

TABLE 1

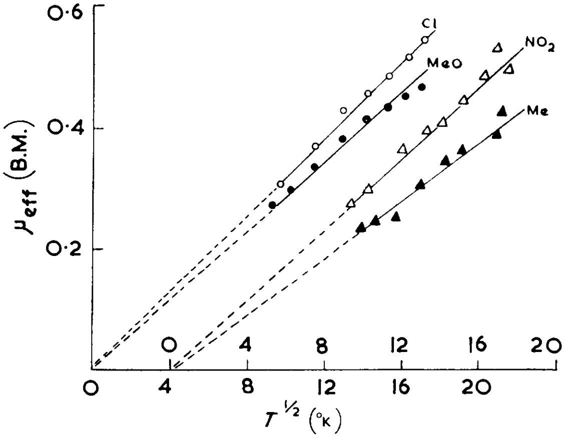
Nitric oxide uptake in the preparation of the mononitrosyls, and their molar conductances and magnetic moments at 293°K

Substituent	Moles of NO absorbed * per g.-atom of Co	Solvent	Λ_M in †, ‡ nitrobenzene (mhos cm.^{2})	μ_{eff} (Bohr magnetons)
None	1·0, 1·0, 1·1	Chloroform	0·6 §	0·7
3,3′-Dinitro	1·0, 1·0	Dimethylformamide	Insol.	—
5,5′-Dinitro	1·0, 1·0, 0·99	,,	Insol.	0·5
6,6′-Dinitro	1·0	,,	—	—
4,4′-Dichloro	0·96, 0·99	,,	—	0·3
5,5′-Dichloro	1·0, 0·98	,,	~0 ¶	0·6
5,5′-Dimethyl	1·0, 1·0, 0·99	,,	~0	0·4
3,3′-Dimethoxy	1·1	,,	2·1	0·7
5,5′-Dimethoxy	1·0	,,	~0	0·5

* On mixing Schiff's base and cobalt acetate in an atmosphere of NO except for the unsubstituted compound, which was prepared by direct reaction of NO and the cobalt(II) complex in chloroform. † Solutions in dimethylformamide showed a continuous increase in conductance after preparation, but the molar conductance did not approach that expected for a 1 : 1 electrolyte. ‡ 0·001M-solutions. § *M* in nitrobenzene, 400, calc., 355. ¶ *M* in nitrobenzene, 350, calc. 424.

are sufficiently soluble in nitrobenzene for approximate molecular-weight measurements. These showed the compounds to be monomeric, and hence, unless the solvent is co-ordinated, to be five-co-ordinate.

We have found[8] that reaction with nitric oxide is not restricted to these oxygen-carrying compounds. Similar nitrosyls have been prepared from Schiff's bases obtained from acetylacetone, trifluoroacetylacetone, or *o*-hydroxyacetophenone and ethylenediamine; and from salicylaldehyde and many other amines. Nitric oxide also forms similar compounds with other metals of the first transition series.



Variation with $T^{\frac{1}{2}}$ of magnetic moments of 5-chloro- and 5-methoxy- (lower scale) and 5-nitro- and 5-methyl-nitrosyls (upper scale)

Magnetic Measurements.—The compounds exhibited magnetic moments of about 0·5 Bohr magnetons at room temperature (Table 1). In order to determine the source of this small moment, magnetic susceptibility measurements were carried out over the temperature range 90—300°K. The magnetic moments of the 5-methyl-, 5-nitro-, 5-chloro-, and 5-methoxy-substituted compounds (Figure) vary linearly with $T^{\frac{1}{2}}$, and therefore arise from temperature-independent paramagnetism;[9] no unpaired electrons are present, and there is no question of the small paramagnetism arising from an equilibrium between diamagnetic and paramagnetic species in these compounds.

Infrared Spectra.—The absorption frequencies, in the double-bond region, of the

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[8] A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, unpublished work.

[9] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, London, 1960, p. 421.

nitrosyls and their parent cobalt(II) complexes and Schiff's bases, are given in Table 2. Each nitrosyl shows either a medium to strong additional absorption at higher frequency, or, in the 1620 cm.$^{-1}$ region, an absorption broader and more intense than any in the corresponding parent compound. These absorptions have been assigned to the NO stretching vibration. It has not yet been possible to confirm these assignments by using isotopically substituted nitric oxide. From the magnetic measurements, these compounds contain no unpaired electrons, and may be regarded formally as containing NO$^-$ co-ordinated to cobalt(III), or as NO$^+$ co-ordinated to cobalt(I). The nitrosyl frequencies vary considerably with substituent, but are all at the lower end of the frequency range usually ascribed [10] to co-ordinated NO$^+$, so that the latter formulation is perhaps nearer to the truth. However, the charge distribution must vary according to the amount of double bonding between the metal and the nitric oxide, and the assignment of formal oxidation states is difficult.

TABLE 2

Infrared absorptions (cm.$^{-1}$) in the double-bond region of nitrosyls, parent complexes, and Schiff's bases. The asterisk shows the absorptions assigned to the nitric oxide stretching frequency. σ_p and σ_m are the Hammett substituent constants.[12]

Substituent	Nitrosyl	Parent complex	Schiff's base	σ_p	σ_m
None	* 1624vs	1613m	1634s	0	0
	1596m	1595sh	1610m		
			1577s		
	1531m	1536m	1495s		
3,3′-Dinitro	* 1667s		1653s	—	—
	1637s	1618m	1616m		
	1595m	1605m			
	1538m	1543m	1531s		
	1504m	1506s			
5,5′-Dinitro	* 1696m			1·27	0·710
	1629m	1658w	1642s		
	1597m	1597m	1610s		
	1550m	1550m	1538s		
6,6′-Dinitro	* 1667m	—		—	—
	1639s				
	1621s		1626s		
	1605m		1577m		
	1518s		1520s		
4,4′-Dichloro	1686s			0·227	0·373
	1637s				
	1621s		1626m		
	1592s	1597s	1597w		
		1580sh	1570m		
	1520m	1524m			
5,5′-Dichloro	* 1638s	1639vw	1634s	0·227	0·373
	1621s	1597m	1567m		
	1522m	1515m			
5,5′-Dimethyl	* 1614s	1618m	1639m	−0·170	−0·069
		1595m	1587m		
	1527m	1529m			
3,3′-Dimethoxy	* 1635vs	1639w	1634s	—	—
	1603m	1605m	1580w		
	1539w	1536w			
5,5′-Dimethoxy	* 1631vs		1642m	−0·268	0·115
		1597m	1613w		
	1536m	1534s	1592m		

Substituent Effects on Nitric Oxide Stretching Frequencies.—Variations in the stretching frequencies of co-ordinated CO and NO groups are usually considered to reflect changes in the amount of metal-ligand double-bonding [11] necessary to maintain an approximately neutral metal atom. Thus, electron-withdrawing substituents increase the nitrosyl

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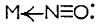
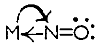
[10] J. Lewis, *Sci. Prog.*, 1959, **47**, 508.
[11] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 292.

stretching frequencies with respect to the unsubstituted compound, presumably by increasing the contribution of (a):



$M \leftarrow N \equiv O\colon$

(a)



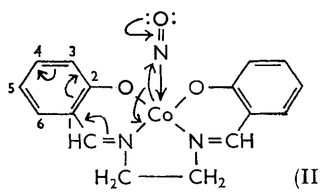
$M \leftarrow N = \ddot{O}\colon$

(b)

The overall trend in the NO stretching frequencies, with 4,4′- and 5,5′-substituents particularly, seems too large to be due to coupling effects, because of the remoteness of the NO group. Solution studies were impossible, because of solubility difficulties. However, solid-state interactions are usually small with groups of high bond-order.

Substituent effects can be transmitted to the metal *via* the co-ordinated oxygen and/or nitrogen atoms. 5,5′-Substituents seem to act more through the oxygen atom *para* to themselves, since there is an approximately linear relationship (except for the 5,5′-dimethoxy-compound) between the Hammett constants[12] for *para*-substituents and the NO stretching frequency. There is, at most, a rough correlation with *meta*-constants σ_m or with $\sigma_p + \sigma_m$. This may be expected, since electron density changes reach the *meta*-position inductively, are smaller, and their effects tend to be damped out (compared with those being transmitted through oxygen) because of the additional atom between the ring and the metal.

Compared with the 5,5′-substituted compounds, the 4,4′-dichloro-substituted compound shows a very high NO stretching frequency. It seems possible that electron-withdrawing substituents in this position are conjugated through the metal to the NO group (II), and can affect this absorption considerably. 5,5′-Substituent-effects are less marked because of the lack of suitable orbitals on the oxygen atom for π-bonding with the metal.



(II)

The 3,3′- and 6,6′-substituents exert smaller, but similar effects. Models show that nitro-groups in these positions are no longer coplanar with the aromatic ring, and therefore do not exert their full mesomeric effects. Such substituents might also exert direct effects upon the electronic distribution between the cobalt atom and the nitric oxide molecule, so that only qualitative correlations can be expected.

Methoxy-substituents commonly exhibit $+M$ and $-I$ effects, the former predominating, and often behave anomalously in σ correlations.[13] In this system only the $-I$ effect appears to be operating. Both 3- and 5-methoxy-substituents are *meta* with respect to the $-HC=N<$ grouping. The Hammett σ-constants show that methoxy-groups decrease the electron density at *meta*-positions ($\sigma_m = +0{\cdot}115$) and increase that at *para*-positions ($\sigma_p = -0{\cdot}268$). Because of the lack of suitable metal orbitals, electron-release to the cobalt atom *via* the phenolic oxygen atom and thence to the co-ordinated nitric oxide is somewhat inhibited compared with electron-withdrawal *via* the $-HC=N<$-group. Hence it is reasonable that the $-I$ effect of the methoxy-group should predominate.

Ligands such as carbon monoxide and nitric oxide are usually considered to form such weak σ-bonds to metals that the main strength of the bond arises from the back-donation. This seems to be confirmed by the substituent effects: were σ-bonding important, electron-attracting substituents would be expected to reduce the $N \sim O$ bond order and the nitric oxide stretching frequency, the reverse of what is found.

Structure.—All *X*-ray investigations of complexes containing quadridentate ligands of this type so far reported show the ligand to take up an essentially planar arrangement around the metal atom.[3,5,14] It would seem likely that these nitrosyls have the square-pyramidal structure (II). The axis of the nitric oxide molcule may be at right-angles to the

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[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, ch. VII.

[13] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[14] T. N. Waters, D. Hall, and F. J. Llewellyn, *Chem. and Ind.*, 1958, 1203; D. Hall and F. H. Moore, *Proc. Chem. Soc.*, 1960, 256; D. Hall and T. N. Waters, *J.*, 1960, 2644; K. Pachler and M. V. von Stackelberg, *Z. anorg. Chem.*, 1960, **305**, 286.

plane of the rest of the molecule, or more nearly parallel to it, as with the analogous compound bis(dimethyldithiocarbamato)nitrosylcobalt.[15] In the latter situation, the changes in the nitric oxide stretching frequency with substituent can be explained on the assumption of concomitant changes in the amount of double-bonding from filled metal orbitals to empty antibonding orbitals on the nitric oxide molecule.

EXPERIMENTAL

The salicylaldehydes were obtained commercially or prepared by standard methods. The Schiff's bases were prepared by condensation of the aldehydes with ethylenediamine in ethanol; they were crystallised from ethanol or dimethylformamide. Cobalt acetate was recrystallised from dilute acetic acid. Dimethylformamide was dried with barium oxide and distilled in nitrogen under reduced pressure; it was stored under nitrogen. Dimethylformamide has the advantages that vapour-pressure corrections were unnecessary in the measurement of the nitric oxide uptake at room temperature, and that cobalt acetate and the Schiff's bases are moderately soluble in it. The cobalt(II) complexes and the nitrosyls were less soluble, and usually separated readily. Cobalt was estimated by a back-titration method with e.d.t.a. The complexes were previously destroyed by heating them with a mixture of oxidising acids.

Preparation of Cobalt(II) *Complexes.*—In order to make the assignments of the nitric oxide stretching absorptions more certain, particularly those occurring in the 1600 cm.$^{-1}$ region, where aromatic absorptions occur, the corresponding cobalt(II) compounds were prepared.

NN'-ethylenebis(salicylideneiminato)cobalt(II) and its 3-methoxy-derivative were prepared as described in Part I.[1]

The remaining compounds were prepared by mixing hot, equimolar dimethylformamide solutions of the appropriate Schiff's base and cobalt acetate. In this solvent, these compounds oxidised so readily that it was necessary to filter and wash the usually crystalline products in an atmosphere of nitrogen: (Found for 5-nitro-derivative: Co, 14·0. Calc. for $C_{16}H_{12}N_4O_6Co$: Co, 14·2%. Found for 3-nitro-derivative: Co, 14·3%. Found for 5-methyl-compound: Co, 16·7. Calc. for $C_{18}H_{18}N_2O_2Co$: Co, 16·7%. Found for 5-methoxy-compound: Co, 15·2%. Calc. for $C_{18}H_{18}N_2O_4Co$: Co, 15·3%). The 4-chloro- (Found: C, 49·7; H, 3·4; N, 6·9; Co, 15·2. $C_{16}H_{12}N_2O_2Cl_2Co$ requires C, 48·75; H, 3·1; N, 7·1; Co, 15·0%) and 5-chloro-derivative (Found: C, 49·35; H, 3·5; N, 6·7; Co, 14·7%) are new.

The 5-methyl-, 5-methoxy-, and 4-chloro-compounds did not change colour on exposure to oxygen at 1 atm. pressure, but the other compounds turned black and absorbed variable amounts of oxygen; the original colour could be restored by heating the compounds under reduced pressure. The oxygen-carrying capacity of the 5-nitro-compound was considerably greater (2·4% increase in weight) than that (1·5%) found by Bailes and Calvin [16] for this compound obtained from pyridine or n-propanol. At higher oxygen pressures, it would probably absorb the theoretical one molecule of oxygen per two cobalt atoms (3·9%).

Reactions with Nitric Oxide.—Nitric oxide was generated by mixing aqueous solutions of acidified ferrous sulphate and sodium nitrite, and purified by passage through a solid carbon dioxide–alcohol trap and a tower containing pellets of potassium hydroxide.

The Schiff's base and the cobalt acetate (a few per cent in excess of an equimolar quantity) were dissolved separately in dimethylformamide, the total volume of solvent being about 25 ml. After equilibration, the solutions were mixed in an atmosphere of nitric oxide at room temperature, and stirred magnetically; the solution darkened as the nitric oxide was rapidly absorbed. The volume absorbed was measured with a gas burette. In a few cases, the previously prepared cobalt–Schiff's base complex was added to the solvent in an atmosphere of nitric oxide; crystals of the nitrosyls soon separated. When the absorption of nitric oxide had ceased, usually after 2—3 hr., the nitric oxide above the solution was replaced by nitrogen, and the nitrosyl filtered off, washed rapidly, and dried at room temperature. When dissolved in dimethylformamide, these nitrosyls are gradually oxidised by air but, provided that the crystals are rapidly filtered from the mother-liquor and quickly washed with water and a volatile solvent, this is not important. Yields of 50—60% were obtained. It was later found that powdered cobalt acetate could be added to the solution of Schiff's base without detriment to the product. This reduced the volume of dimethylformamide necessary and increased the yields to 80—90%.

[15] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J.*, 1962, 668.

[16] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

NN′-*Ethylenebis(salicylideneiminato)nitrosylcobalt*.—This was the only compound obtained pure by direct reaction of the cobalt(II) complex with nitric oxide. The unsubstituted cobalt(II) complex, previously heated under reduced pressure to remove absorbed oxygen, was added to chloroform (25 ml.) under nitric oxide. The black, crystalline *compound* was crystalllised from chloroform (Found: C, 53·9; H, 4·0; N, 11·4; Co, 16·5. $C_{16}H_{14}N_3O_3Co$ requires C, 54·1; H, 4·0; N, 11·8; Co, 16·6%). It was unchanged in air.

NN′-*Ethylenebis-(3-methoxysalicylideneiminato)nitrosylcobalt*.—This *compound* was a dark brownish green powder, stable to air (Found: C, 52·2; H, 4·1; N, 10·0; Co, 14·2. $C_{18}H_{18}N_3O_5Co$ requires C, 52·0; H, 4·4; N, 10·1; Co, 14·2%). The direct reaction of the dehydrated cobalt(II) complex with nitric oxide did not give a pure product. This method was tried unsuccessfully with acetonitrile, chloroform, cyclohexane, dimethylformamide, and pyridine. Approximately an equimolar amount of nitric oxide was rapidly absorbed, except in cyclohexane (0·4 mole). In pyridine, the reaction continued slowly and indefinitely beyond the absorption of 1 mole but a reasonably pure product was obtained by stopping the reaction at this point.

NN′-*Ethylenebis-(5-methoxysalicylideneiminato)nitrosylcobalt*.—This *compound* was a green-brown powder (Found: C, 52·1; H, 4·5; N, 9·9; Co, 14·3. $C_{18}H_{18}N_3O_5Co$ requires C, 52·0; H, 4·4; N, 10·1; Co, 14·2%).

NN′-*Ethylenebis-(5-methylsalicylideneiminato)nitrosylcobalt*.—This *compound* was brown in colour (Found: C, 56·5; H, 5·0; N, 10·8; Co, 15·65. $C_{18}H_{18}N_3O_3Co$ requires C, 56·4; H, 5·3; N, 11·0; Co, 15·4%).

NN′-*Ethylenebis-(4-chlorosalicylideneiminato)nitrosylcobalt*.—This *complex* was brown in colour (Found: C, 44·8; H, 3·0; N, 9·6; Co, 13·6. $C_{16}H_{12}N_3O_3Cl_2Co$ requires C, 45·3; 2·9; N, 9·9; Co, 13·9%).

NN′-*Ethylenebis-(5-chlorosalicylideneiminato)nitrosylcobalt*.—The *compound* was a black crystalline solid (Found: C, 44·8; H, 2·9; N, 9·45; Co, 14·0. $C_{16}H_{12}N_3O_3Cl_2Co$ requires C, 45·3; H, 2·9; N, 9·9; Co, 13·9%).

NN′-*Ethylenebis-(3-nitrosalicylideneiminato)nitrosylcobalt*.—This *nitrosyl* was black (Found: C, 42·5; H, 2·7; N, 15·8; Co, 13·0. $C_{16}H_{12}N_5O_7Co$ requires C, 43·1; H, 2·7; N, 15·7; Co, 13·2%).

NN′-*Ethylenebis-(5-nitrosalicylideneiminato)nitrosylcobalt*.—The direct reaction of the cobalt(II) complex with nitric oxide in chloroform, pyridine, or acetonitrile gave indefinite materials. Blue-black crystals of the *compound* were obtained by mixing cobalt acetate and the Schiff's base as above (Found: C, 43·8; H, 3·1; N, 15·5; Co, 13·4. $C_{16}H_{12}N_5O_7Co$ requires C, 43·1; H, 2·7; N, 15·7; Co, 13·2%).

NN′-*Ethylenebis-(6-nitrosalicylideneminato)nitrosylcobalt*.—The *compound* was chocolate-brown (Found: C, 43·2; H, 2·9; N, 15·4. $C_{16}H_{12}N_5O_7Co$ requires C, 43·1; H, 2·8; N, 15·7%).

Physical Measurements.—Conductance measurements were carried out with a Mullard bridge type GM 4140/I. Magnetic-susceptibility measurements were made over the temperature range 90—300°K with apparatus described previously.[17] Owing to the weak paramagnetism of the compounds and the high molecular weights of the ligands, the diamagnetism of the latter was determined experimentally rather than from Pascal's constants. Because of low solubility the compounds could not usually be recrystallised. The linearity of the graph of magnetic moment versus $T^{\frac{1}{2}}$ is an indirect confirmation of the purity of the compounds. Traces of paramagnetic impurities, *e.g.*, cobalt acetate or cobalt(II) complex, would cause marked deviations from linearity, especially at the lower temperatures. Such behaviour occurred with analytically pure samples of the unsubstituted nitrosyl. The infrared spectra of the compounds in Nujol mulls were recorded on a Grubb–Parsons double-beam grating instrument type GS 2A.

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[17] A. Earnshaw, *Lab. Practice*, 1961, **10**, 294.