352. *Studies on Transition-metal–Nitric Oxide Complexes. Part V.* Nitric Oxide Complexes of Tetrahedral Bivalent Nickel and Some Other Metals.*

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Absorption spectra and magnetic susceptibility measurements have been made on the paramagnetic nitrosyl, hydroxy-, and alkoxy-complexes of nickel, and it is suggested that these contain bivalent, tetrahedral nickel. Studies have also been made on a similar complex of iron, and of the complexes $Rh^{-I}(NO)_2Cl$, $Pd^0(NO)_2Cl_2$, and $K[Co^{-I}(CN)(CO)_2NO]$.

This paper is concerned primarily with the paramagnetic nickel nitrosyl hydroxide, previously formulated as $Ni(NO)(OH)(H_2O)_2$, and the corresponding alkoxides. The present studies indicate that these complexes, which have been known for many years, must be formulated as containing tetrahedral bivalent nickel, for example, as $NiNO(OH)_3$, and it seems that they were the first compounds of this type to be prepared, although not recognised as such; other tetrahedral complexes of bivalent nickel have only recently been unambiguously proved.[1]

(1) *Nitric Oxide Hydroxy- and Alkoxy-complexes of Nickel.*—Shortly after the discovery of nickel tetracarbonyl, Berthelot [2] showed that nitric oxide reacted with the carbonyl in the vapour phase to give an ill-defined, blue, volatile product, to which the formula $Ni(NO)_2$ was later assigned by Mond and Wallis.[3] The complex and its " alcoholate " derivatives were studied later by Reihlen *et al.*,[4] by Frazer and Trout,[5] and, more intensively, by Anderson.[6,7] The present position is summarised by Emeléus and Anderson.[8]

Study of the nickel nitrosyl hydroxide is difficult owing to its extreme instability. According to Anderson,[7] the most representative formulation is $Ni(NO)(OH)(H_2O)_{1\cdot5}$ or $Ni(NO)(OH)(H_2O)_2$. It is prepared by passing nitric oxide into nickel carbonyl, either alone or in an inert solvent. Traces of water are necessary,[6] but too much water results in the formation of $Ni(OH)_2$; as a result of this, the yields of the reaction are very low. The complex dissolves in air-free water to a deep blue basic solution which decomposes within a few seconds; it is also soluble in alcohols, but not in benzene, chlorobenzene, nitrobenzene, or chloroform.

Anderson suggests [6,7] that the complex is $Ni(NO)(OH)(H_2O)_n$ ($n = 1$ or 2) containing univalent nickel. If this formula were correct, with NO donating as NO^+,[9] the nickel atom would formally be Ni^0, and the compound should be tetrahedral and diamagnetic, it being assumed to be monomeric. Anderson favoured univalent nickel since silver nitrate was apparently reduced. We have found that, in fact, silver oxide is formed owing to the basic nature of the solutions and not silver.

Magnetic measurements made over a temperature range (Table 1) show, however, that the complex has a moment of 2·97 B.M. with a large negative Curie temperature of −59°.

The infrared spectrum (Table 2) shows a strong peak at 1828 cm.$^{-1}$, typical of a co-ordinating NO^+ group.[9] There is also a strong OH peak near 3500 cm.$^{-1}$ but only weak

* Part IV, *J.*, 1959, 872.

[1] Venanzi, *J.*, 1958, 719.
[2] Berthelot, *Compt. rend.*, 1891, **112**, 1243.
[3] Mond and Wallis, *J.*, 1922, **121**, 33.
[4] (*a*) Reihlen, Gruhl, von Hessling, and Pfrengl, *Annalen*, 1930, **482**, 161; (*b*) Reihlen, *Z. anorg. Chem.*, 1937, **230**, 223.
[5] Frazer and Trout, *J. Amer. Chem. Soc.*, 1936, **58**, 2201.
[6] Anderson, Thesis, University of London, 1932.
[7] Anderson, *Z. anorg. Chem.*, 1936, **229**, 357.
[8] Emeléus and Anderson, " Modern Advances in Inorganic Chemistry," Routledge and Paul, London, 1952, p. 433.
[9] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

absorption at 1630 cm.$^{-1}$; on Anderson's formulation strong absorption in the 1600 cm.$^{-1}$ region would be expected.

TABLE 1. *Magnetic measurements on* $Ni^{II}(NO)(OH)_3$ *(solid).*

T (°K)	297·5	265·5	248·0	227·5	204·0	168·0	135·5	114·5
χ_A (c.g.s.u. × 10^{-3})	3·08	3·46	3·65	3·82	4·23	4·91	5·65	6·06

Diamagnetic correction: -26×10^{-6} c.g.s.u.

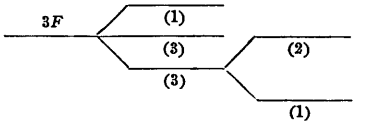
TABLE 2. *Infrared spectra.* (All in Nujol mulls.)

Compound	NO assigned frequency (cm.$^{-1}$)	Other strong bands (cm.$^{-1}$)
$Ni(NO)(OH)_3$	1828 (s)	3500
$Ni(NO)(OMe)_2OH$	1820 (s)	3500, 1030
$Ni(NO)(OEt)_2OH$ ..... / $Ni(NO)(OEt)(OH)_2$	1820 (s)	3500, 1040
n-Propanol complex	1820 (s)	3500, 1050, 1010, 960
n-Butanol complex	1815 (s)	3500, 1240, 1050
$[Ni(NO_2)(OMe)(MeOH)]_2$	—	3500, 1410, 1270, 1030, 845
$Ni(NO_2)$-ethoxy-complex	—	3500, 1410, 1270, 1030, 845
$Fe_2(NO)_2(MeOH)_2(OMe)(OH)$	1752 (s)	3500, 1055, 1015
$Pd(NO)_2Cl_2$	1833 (s), 1818 (s)	—
$Rh(NO)_2Cl$	1703 (s), 1605 (s)	—
$K[Co(CN)(CO)_2(NO)]$	1720 (s)	2102, 2037, 1960

The methanolic solution of the hydroxy-complex (which will probably then exist as the methoxy-derivative described below) shows a strong absorption peak in the visible spectrum at 650 mμ, but no peak near 400 mμ.

The above facts lead to the conclusion that the complex contains either tetrahedral or octahedral bivalent nickel. Although it is not possible to obtain a molecular weight for either the nitrosyl hydroxide or the nitrosyl alkoxides, the blue colour of these species and the absence of a peak at 410 mμ are indicative of tetrahedral bivalent nickel complexes;[10] tetrahedral nickel complexes,[11,12] such as the $[NiCl_4]^-$ ion, are also known to absorb at 650 mμ.

The magnetic moment of the complex, 2·97 B.M., is in agreement with the value obtained by Venanzi [1] for the tetrahedral triphenylphosphinenickel derivatives, but is substantially lower than the value obtained by Nyholm *et al.*[12] for the tetrahalide derivatives of nickel. The ^3F state of nickel in a tetrahedral state will be split by a cubic crystalline field into two low-lying orbital triplets and a singlet level. This should then give rise to an appreciable orbital contribution, as found in the tetrahalides. If, however, a field of low symmetry is also present, the lowest triplet will be further split into a singlet and a doublet (see Figure). The orbital contribution can then be considerably reduced if the singlet–



doublet separation is large compared with kT because the orbital contribution is effectively quenched in the singlet if the doublet is of the order of 2000 cm.$^{-1}$ higher. This system is then analogous to V^{3+} complexes in an octahedral environment where splittings of this order are assumed to occur in the case of the vanadium alum.[13] A field of symmetry lower than cubic is probably present in both the triphenylphosphine- and the nitrosyl-hydroxy-nickel complex because of their unsymmetrical structures. However, the large value obtained for the Curie–Weiss constant may imply that there is antiferromagnetic interaction occurring in the nitrosyl hydroxy-complexes.

[10] Katzin, *Nature*, 1958, **182**, 1013.
[11] Weyl, "Quelques problèmes de chimie minérale," X Solvay Conseil de Chimie, Brussels, 1956, p. 420.
[12] Gill, Nyholm, and Pauling, *Nature*, 1958, **182**, 168.
[13] van der Handel and Siegert, *Physica*, 1937, **4**, 871.

The methoxy-complex,[4,6,7] previously formulated as $Ni(NO)(OH)(MeOH)_2$ is prepared by the action of dry nitric oxide on methanolic nickel tetracarbonyl.[4] Anderson [6,7] concluded that it was best formulated as $Ni(NO)(OH)(MeOH)_2$, although he pointed out that the analyses [6] better fitted the formula $Ni(NO)(OH)(OMe)_2$, which we now accept as correct. Since the infrared NO^+ stretching frequency (Table 2) and magnetic susceptibility (Table 3) are substantially the same as for $Ni(NO)(OH)_3$, it seems clear that the latter structure is probably the correct one.

Anderson also prepared in ethanolic solution a complex which he formulated as $Ni(NO)(OEt)(H_2O)$. We have re-examined this (Tables 2 and 3); it is clearly of the same

TABLE 3. *Magnetic susceptibility measurements on alkoxides at 22°.*

Complex	χ_g (c.g.s.u. $\times 10^{-5}$)	$\mu_{eff.}$ (B.M.)	Diamagnetic corrections (c.g.s.u. $\times 10^{-6}$)
$Ni(NO)(OH)(OMe)_2$	1·94	2·8	50
$Ni(NO)(OEt)_2OH$ + $Ni(NO)(OEt)(OH)_2$	1·96	2·8	80
$[Ni(NO_2)(OMe)(MeOH)]_2$	4·2	3·3	43
$Fe_2(NO)_2(OMe)(OH)(MeOH)_2$	2·88	2·97	40

structure as the methoxide, but the analyses do not fit the formulation $Ni(NO)(OH)_2(OEt)$. We suggest that it is in fact a mixture of $Ni(NO)(OH)(OEt)_2$ and $Ni(NO)(OH)_2(OEt)$. Since it is not possible to recrystallise these compounds, it is difficult to confirm this point; separation by chromatography might be possible, but the compounds are sensitive to air and are spontaneously transformed into the green nitro-form (see below), so that this would be technically difficult.

We have also prepared similar complexes with *n*-propyl, *n*-butyl, and *n*-pentyl alcohols (Table 2). They are all considered to have structures similar to $Ni(NO)(OMe)_2(OH)$, but analyses are variable owing to the increasing instability of the complexes as the alcoholic chain-length increases. They may all be regarded as mixtures of complexes of the form $Ni(NO)(OR)_n(OH)_{3-n}$.

The deep blue $Ni(NO)(OMe)_2(OH)$ changes [4,6,7] spontaneously in the course of a day to a green complex which, though it had the same analytical composition, had no reducing power. No gas is evolved or absorbed during the change. We have noted the same phenomenon in the blue ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol complexes, although the change is slower the greater the chain length of the alcohol.

Anderson [7] suggested that, in view of the loss of reducing power of nickel, a hyponitrite complex is formed (cf. $[Co(NH_3)_5NO]_2Cl_4$). A recent study of such complexes [14] has shown that a characteristic infrared absorption band is observed in the 1000—1200 cm.$^{-1}$ region; no such bands arise in these green nickel complexes.

However, we have observed that the NO^+ band at 1820 cm.$^{-1}$ disappears in the green complexes, and is replaced by strong bands at 845 and 1270 cm.$^{-1}$ together with a weaker band at 1420 cm.$^{-1}$. Such absorption is characteristic of bridging nitro-groups.[15] Magnetic measurements (Table 3) show that the complex retains two unpaired electrons. The visible absorption spectrum shows a strong peak at 470 mμ.

It therefore seems likely that the green complexes are formed by a reaction of the type known to occur in nitroprussides,[16] and which is believed to occur in certain nitrosyl-platinum complexes:[17]

$$NO^+ + OH^- \longrightarrow NO_2^- + H^+$$

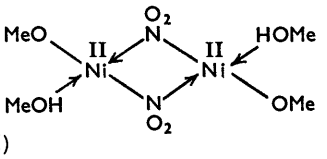
so, in this case the reaction is

$$Ni(NO)(OH)(OMe)_2 \longrightarrow Ni(NO_2)(OMe)(MeOH)$$

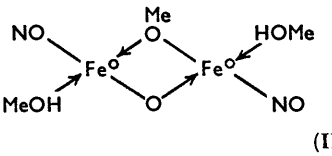
[14] Griffith, Lewis, and Wilkinson, *Physica*, 1937, **4**, 38.
[15] Nakamoto, Fujita, and Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.
[16] Cambi and Szego, *Atti R. Accad. Lincei*, 1927, **5**, 737; Hantzsch, *Z. phys. Chem.*, 1909, **65**, 57.
[17] Lewis, unpublished observations.

We can hence write the structural unit for the complex as (I), which will have analyses identical with those of the blue complex, as is found. The green colour of the complex both in the solid state and in methanolic solution indicates octahedral co-ordination of the metal atom; in the solid this could be achieved by further polymerisation through methoxy-bridges.

(2) *Dimethanol-μ-hydroxy-μ-methoxydinitrosyldi-iron*(0).—$Fe_2(NO)_2(OMe)(OH)(MeOH)_2$ was first prepared by Manchot and Gall [18] and formulated by them as $Fe(NO)(MeOH)_2$. It was later examined by Reihlen *et al.*[4a] who, after extensive analyses, assigned the formula $Fe_2(NO)_2(MeOH)_3OH$. As with the nickel compounds, the extreme instability of the complex renders precise measurements difficult. Infrared spectra (Table 2) show the presence of only one NO^+ stretching frequency and magnetic susceptibility measurements made at room temperatures on several samples (Table 3) indicate the presence of two unpaired electrons. From this evidence, the most reasonable formulation is (II), with tetrahedral (sp^3) zerovalent iron. Attempts were made to prepare analogues of this with higher alcohols, but only the ethanol complex could be isolated. It was less stable than the methoxide, but had a similar infrared spectrum. It was too unstable to permit reliable measurements.



(I)



(II)

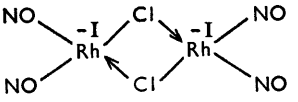
It is interesting to compare the paramagnetism of these complexes with the diamagnetism that occurs in Roussin's red series of compounds which have bridging sulphur atoms. In the latter, the iron atom has a formal valency of −1 and the odd electron on each iron atom is paired to give a diamagnetic complex. The Fe–Fe bond distance in the ethyl ester is 2·72 Å,[19] which is longer than can be expected for a Fe–Fe single bond, $Fe_2(CO)_9$ being taken as an example (Fe–Fe = 2·46 Å). If we assume that the spin-coupling operates through the bridging sulphur atoms, presumably owing to the participation of the 3*d* orbitals of sulphur, the paramagnetism of the oxygen-bridged system is understandable since with oxygen the suitable *d* orbitals are, of course, inaccessible.

(3) *Nitric Oxide–Halide Complexes of Palladium and Rhodium.—Palladium*(0) *dinitrosyl dichloride*, $Pd(NO)_2Cl_2$. This dichloride, and the disulphate, was prepared by Manchot and Waldmüller [20] by passing nitric oxide into methanolic palladous chloride or sulphate. It is unstable, evolving nitric oxide at high temperatures or in moist air. We have found it to be diamagnetic and to show two peaks in the NO^+ stretching region (Table 3). The most reasonable structure is hence $Pd(NO)_2Cl_2$, which involves Pd^0 with sp^3 tetrahedral bonding, and is thus related to the nitrosyl hydroxy-complexes of nickel. The instability of the complex is understandable on the grounds of the monomeric nature and low valency of the metal atom.

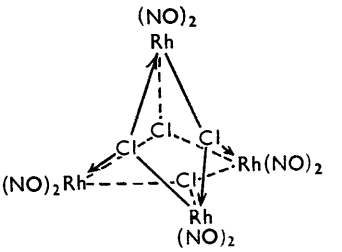
Rhodium(−I) *dinitrosyl chloride*, $Rh(NO)_2Cl$. This was first prepared by Manchot and König [21] by passing dry nitric oxide at 60° over $Rh(CO)_2Cl$ for 2 days. The resulting black substance he formulated as $RhO,3NO,RhCl_2$. We have examined the magnetic susceptibility and infrared spectra of this complex. The analyses which we obtain closely fit the stoicheiometry $Rh(NO)_2Cl$. It is diamagnetic, and the infrared spectrum in a mull shows two peaks in the NO^+ stretching region (Table 2). It is unreactive and is insoluble in water and most other solvents; attempts to sublime it result in decomposition. These facts suggest that the compound is polymeric and may have one of the structures (III) or (IV). Both would give two infrared-active NO^+ stretching frequencies and both would

[18] Manchot and Gall, *Annalen*, 1929, **470**, 271.
[19] Thomas, Robertson, and Cox, *Acta Cryst.*, 1958, **11**, 599.
[20] Manchot and Waldmüller, *Ber.*, 1926, **59**, 2363.
[21] Manchot and König, *ibid.*, 1927, **60**, 2130.

make the rhodium diamagnetic. The first structure is analogous to that of $[Co(NO)_2I)]_2$.[22] The second, involving five-co-ordination for the metal atom, is the analogue of $[Ni(NO)I]_4$;[23] such a halogen-bridged structure has been proved for the complexes $[Cu(AsL_3)I]_4$.[24]



(III)



(IV)

The insolubility and general inertness of the rhodium complex favour the latter structure, so we suggest it for the compound.

(4) *Nitric Oxide Cyano-complex of Cobalt.—Potassium cyanonitrosyldicarbonylcobaltate-(−1),* $K[Co(CN)(NO)(CO)_2]$. This was prepared by Nast and Rohmer [25] from potassium cyanide and cobalt carbonyl nitrosyl. It is diamagnetic.[25] There are two possible structures: square planar (dsp^2) hybridisation of the cobalt, in which case the complex would be isoelectronic with $[Co^{I}(CN)_3CO]^{2-}$,[26] with NO donating as NO^-, as in $[Co(CN)_5NO]^{3-}$;[14] or tetrahedral (sp^3) hybridisation, with the complex isoelectronic with $Co^{I}(CO)_3NO$ and $Co^{-I}(CO)_4H$ (NO donating as NO^+). That the latter is the correct structure is shown by the presence of an intense NO^+ stretching frequency, together with one CN and two CO such frequencies (Table 2).

Experimental

The nitric oxide hydroxy- and alkoxy-nickel *complexes* were prepared as described by Anderson. His extensive analyses for the hydroxide and methoxide fit the revised formulation [Found: Ni, 44·1; N, 10·2. $Ni(NO)(OH)_3$ requires Ni, 42·0; N, 10·0%. Found: Ni, 35·2; N, 7·7; C, 14·5; H, 4·4. $Ni(NO)(OMe)_2OH$ requires Ni, 35·0; N, 8·4; C, 14·3; H, 4·2%]. For the ethoxide, a mixture of $Ni(NO)(OEt)(OH)_2$ and $Ni(NO)(OEt)_2(OH)$ in the ratio 5 : 1 is suggested by the analyses (Found:[6] Ni, 38·0; N, 9·6; O, 16·0; H, 4·0. Calc.: Ni, 35·0; N, 8·2; C, 15·8; H, 4·1%). The high values for nickel are almost certainly due to traces of $Ni(OH)_2$,[6] to which these complexes very readily decompose.

$Fe_2(NO)_2(MeOH)_2(OMe)(OH)$ was prepared by Reihlen and his collaborators' method,[4a] and the new formulation fits the original analyses (Found: Fe, 39·8; C, 13·0; N, 10·0; H, 3·5. Calc.: Fe, 39·6; C, 12·8; N, 9·9; H, 3·6%).

$Pd(NO)_2Cl_2$ was prepared according to Manchot and Waldmüller [20] (Found: Pd, 44·9. Calc.: Pd, 44·3%). $Rh(NO)_2Cl$ was prepared according to Manchot and König [21] and re-analysed [Found: Rh, 50·9; Cl, 18·5; NO, 30·8. Calc. for $Rh(NO)_2Cl$: Rh, 50·6; Cl, 17·9; NO, 30·25%].

$K[Co(CN)(CO)_2(NO)]$ was prepared as by Nast and Rohmer.[25]

Physical Measurements.—Infrared spectra were measured on a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride and calcium fluoride optics. Absorption spectra were taken on a Perkin-Elmer recording spectrophotometer, model 4000. Magnetic susceptibilities were measured on solid samples on a Gouy balance.

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Imperial College, London, S.W.7. [*Received, December 23rd,* 1958.]

[22] Hieber, Beck, and Jahn, *Z. Naturforsch.*, 1958, **13**b, 194, 196.
[23] Hieber and Nast, F.I.A.T. Review of German Science 1939—1946, Inorganic Chemistry, Part II, 146.
[24] Mann, Purdie, and Wells, *J.*, 1936, 1503.
[25] Nast and Rohmer, *Z. anorg. Chem.*, 1956, **285**, 271.
[26] Hieber and Bartenstein, *ibid.*, 1954, **276**, 1.