168. *Studies on Transition-metal–Nitric Oxide Complexes. Part VI.* Platinum, Palladium, and Nickel Complexes.*

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Several new six-co-ordinate nitric oxide complexes of platinum(II) and palladium(II) and four- and six-co-ordinate nickel(II) complexes are reported.

The infrared criterion for co-ordination of nitric oxide to a transition metal as an NO$^-$ group, a band at *ca.* 1100 cm.$^{-1}$, has been confirmed by isotopic substitution.

THIS paper is concerned with nitric oxide complexes of platinum(II), palladium(II), and nickel(II). The new compounds together with their infrared spectra are listed in Table 1.

Since several of the complexes could have been formulated with NO$^-$ rather than NO$^+$ co-ordination, we have also attempted by use of ^{15}N as tracer to confirm that such NO$^-$ complexes show a weak to moderately strong peak in the region of 1100 cm.$^{-1}$.

TABLE 1. *Infrared spectra (cm.$^{-1}$) of* Pt–, Pd–, *and* Ni–*nitric oxide complexes.*

Complex	NO stretch	Other strong bands
$K_2[Pt(NO)Cl_5]$ *	1711	—
$Na_2[Pt(NO)Cl_5]$ †	1765	—
$K_2[Pt(NO)(CN)_5]$ †	1720	2110 (CN)
$K_2[Pt(NO)(NO_2)_4Cl]$ *	1720	1320 and 835 (NO_2)
$K_2[Pt(NO)(NO_2)_4(NO_3)]$ *	1775	1350 and 840 (NO_2); 1500, 1260, 970, 940 and 815 (NO_2)
$Cs_2[Pt(NO)(NO_2)_4(NO_3)]$ *	1720	
$[Pt(NO)(en)_2Cl]Cl_2$ †	1750	1645, 1590 and 1300 (en)
$[Pt(NO)(NH_3)_4Cl]Cl_2$	1670	1620, 1530, 1330, and 910 (NH_3)
$[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$ *	1725	1615, 1560 (NH_3); 1040, 940, 825 (NO_3)
$[Pt(NO)(NH_3)_4(OAc)]Cl_2$ *	1690	1560, 1500, 900, 820 (NH_3 and OAc^-)
$[Pt(py)_2(NO_2)Cl]$	—	1300, 830, and 825 (NO_2); 1620, 1210, 1150, 1065, and 760 (py)
$(pyH)_2[PtCl_4]$	—	1610, 1210, 1060, and 760 (py)
$[Pt(NH_3)_2Cl_4]$	—	1620, 1590, 1240, 900 (NH_3)
$[Pt(NH_3)_4(SO_4)]Cl_2$ *	—	1620, 1590, 1240 (NH_3); 1080 (SO_4)
$K_2[Pd(NO)(NO_2)_4(NO_3)]$ *	1720	1300 and 800 (NO_2); 1500, 1280, 1010, 995, and 790 (NO_3)
$[Pd(NO)_2(NO_3)_2]$ †	1810, 1780	1500, 1300, 990, 820 (NO_3)
$[Ni(NO)(NH_3)_2(OH)](OH)_2$ *	1780	3500 (OH); 1615 (NH_3)
$[Ni(NO)(NH_3)(OCH_3)(OH)](OH)$ *	1785	3500 (OH); 1615 (NH_3)
$[Ni(NO_2)(OH)(MeOH)]_2,2H_2O$ *	—	3500 (OH); 1630, 1030, 790 (MeOH); 1410, 1250, 830 (NO_2)

All spectra taken in Nujol mulls.
* New compounds prepared in this work. † Not pure.
en = ethylenediamine; OAc = acetate; py = pyridine.

(A) *Platinum Complexes.*—The only nitric oxide complexes of platinum studied previously are

$K[Pt(NO)Cl_3]$,[1] $[Pt(NO)pyCl_2]$,[1] $[Pt(NH_3)_4][Pt(NO)Cl_3]_2$,[1] $[Pt(NO)(NH_3)_4Cl]Cl_2$,[2-4]

and an ill-defined series of products such as $[Pt(NO)(NH_3)_3(HSO_4)_{1\cdot5}(SO_4)_{0\cdot5}Cl_{0\cdot5}]$.[4]

(a) *The action of nitric oxide on aqueous solutions of potassium chloroplatinate*(II). It was reported by Gelman and Maximova [1] that nitric oxide, when shaken with a neutral solution of potassium chloroplatinate(II), gave a green complex (not isolated) which they formulated as $K[Pt(NO)Cl_3]$. It was claimed that this could be precipitated, by addition of

* Part V, *J.*, 1959, 1775.

[1] Gelman and Maximova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 748.

[2] Hadow, *J.*, 1866, **19**, 345.

[3] Jensen, 5th Nord. Kemikermøde Forh., 1939, 200.

[4] Koefoed, "Om nogle Nitroso Platinammoniakforbindelser," Akad. Afh. Kopenhagen, 1894, pp. 32, 500.

tetrammineplatinum(II) chloride, as $[Pt(NH_3)_4][Pt(NO)Cl_3]_2$, or by addition of pyridine to give $[Pt(NO)pyCl_2]$.

These experiments have been repeated. Neutral or acidic aqueous solutions of potassium chloroplatinate(II) slowly absorbed nitric oxide over a period of 24 hours, to give deep-green solutions. Alkaline solutions (pH >9) did not absorb the gas.

Addition of pyridine to the green solution gave yellow dipyridinenitrochloroplatinum(II), $[Ptpy_2(NO_2)Cl]$. This substance was diamagnetic, and its infrared spectrum has strong peaks in the nitro-region (825 and 1300 cm.$^{-1}$),[5] but no nitrosyl absorption bands. It therefore seemed likely that the equilibration, $NO^+ + OH^- \rightleftharpoons NO_2^- + H^+$, observed in nitroprussides [6] and in nickelnitrosyl alcoholate complexes [7] had occurred, the equilibrium having been shifted to the right by the strongly basic pyridine. An attempt to reverse the equilibrium by the addition of hydrochloric acid gave the complex $(pyH)_2[PtCl_4]$.

Addition of tetrammineplatinum(II) chloride to the green solution gave a purple, diamagnetic complex for which consistent analyses could not be obtained. The infrared spectrum of this product showed peaks at 825 and 1300 cm.$^{-1}$ and at 1750 cm.$^{-1}$; similar results were obtained with other precipitants such as cæsium chloride and tetraphenylarsonium chloride. It seems likely that the green solution which results from the reaction of nitric oxide with chloroplatinate(II) ion contains a mixture of a nitro- and a nitrosyl complex. However, the presence of a simple salt $K[Pt(NO)Cl_3]$ seems unlikely in view of the diamagnetism of the solution and the precipitated solid, and if this stoicheiometry is correct it would appear more likely that a polymeric species has been obtained.

(b) *The reaction of nitrosyl chloride with platinum*(II) *complexes.* It was found that a solution of nitrosyl chloride in chloroform reacted with a number of four-co-ordinated platinum(II) complexes to give compounds of the general type $[Pt^{II}(NO)X_5]$. The following new complexes were prepared by this method: $K_2[Pt(NO)Cl_5]$, $K_2[Pt(NO)(NO_2)_4Cl]$, and $[Pt(NO)en_2Cl]Cl_2$. Spectral evidence was obtained for the existence of $Na_2[Pt(NO)Cl_5]$ and $Na_2[Pt(NO)(CN)_5]$. There was no reaction, or decomposition followed, when nitrosyl chloride in chloroform was shaken with the following complexes: $K_2[Pt(CNS)_4]$, $[(C_2H_4)PtCl_2]_2$, and R_2PtCl_2, where $R = Ph_3P$, $Pr^n{}_3P$, $Bu^n{}_3P$, or Ph_3As.

These new compounds were made by shaking a suspension of the platinum(II) complexes for 24 hours with nitrosyl chloride in chloroform. The green products decomposed slowly in water to give platinum(IV) complexes. They were diamagnetic, and all showed strong infrared bands near 1700 cm.$^{-1}$, suggesting that the nitric oxide is found as a co-ordinated nitrosonium ion.[8]

These complexes may contain either five- or six-co-ordinated platinum(II), *e.g.*, $K_2[Pt(NO)Cl_5]$ or $K[Pt(NO)Cl_4],KCl$, $[Pt(NO)en_2Cl]Cl_2$ or $[Pt(NO)en_2]Cl_3$. It was impossible, owing to the insolubility of some of the products, to carry out molecular-weight or conductivity determinations. Very few six-co-ordinate platinum(II) complexes have been reported; [9-11] such a structure is favoured, however, for the following reasons: (i) polarographic and conductimetric measurements on the complex $[Pt(NO)(NH_3)_4Cl]Cl_2$, prepared by the action of nitrosyl chloride in chloroform on $[Pt(NH_3)_4]Cl_2$, confirm that this compound contains six-co-ordinated platinum(II) (see below); (ii) an *X*-ray powder photograph of $K_2[Pt(NO)Cl_5]$ showed no lines which could be attributed to KCl; (iii) the alternative formulation of these compounds as six-co-ordinate platinum(IV) complexes with the nitric oxide co-ordinated as NO^- is eliminated by the infrared spectra, the NO^- ligand absorbing near 1100 (see below and ref. 12) and NO^+ near 1800 cm.$^{-1}$.[8]

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[5] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[6] Cambi and Szegö, *Atti R. Accad. Lincei*, 1927, **5**, 737.

[7] Griffith, Lewis, and Wilkinson, *J.*, 1959, 1775.

[8] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[9] Harris, Nyholm, and Stevenson, *Nature*, 1956, **177**, 1127.

[10] Harris, Livingstone, and Reece, *J.*, 1959, 1505.

[11] Brosset, *Arkiv Kemi, Min., Geol.*, 1948, **25**, No. 19.

[12] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

(c) *Nitrosyltetramminechloroplatinum*(II) *dichloride*, $[Pt(NO)(NH_3)_4Cl]Cl_2$. This complex has been prepared [2–4] by the action of nitric oxide on a solution of tetrammineplatinum(II) chloride in moderately strong hydrochloric acid. It may also be prepared, in a manner analogous to that used for the complexes discussed in the last section, by the action of a solution of nitrosyl chloride in chloroform on a suspension of $[Pt(NH_3)_4]Cl_2$. The complex is green and diamagnetic, and is moderately soluble without decomposition in water.

The infrared spectrum of the complex showed a strong peak at 1670 cm.$^{-1}$, attributed to a N–O stretch; no absorption was found near 1100 cm.$^{-1}$ which could be attributed to NO^- or hyponitro-groups. Conductivity measurements in water indicated that the complex was a 2 : 1 electrolyte.

Polarographic reduction of the complex in 0·1N-potassium chloride at the dropping-mercury electrode gave a single, well-defined irreversible cathodic wave ($E_{\frac{1}{2}} = -1{\cdot}05$ v *versus* S.C.E.). The concentration of the complex was proportional to the diffusion current (see Table 2) and, from a comparison of the diffusion current constant, I, with that found for other platinum(II) ammines [13] and also from the value of the half-wave potential, it is clear that the wave corresponds to a reduction of platinum(II) to platinum(0). Since the characteristic three-stepped reduction wave for the nitrosyl ligand, as found in polarography of the nitroprusside ion,[14,15] is not observed here, it seems likely that the reduced product is a platinum(0)–nitrosyl complex {possibly $[Pt(NO)(NH_3)_2Cl]$} rather than metallic platinum. A similar situation has been observed in polarographic reduction of $K_3[Cr(NO)(CN)_5]$.[16] It has been shown [13, 17] that when platinum(II) ammines are reduced at the dropping electrode to platinum metal, no diffusion-current maximum is observed in most cases. The nitrosyl complex, when reduced polarographically in 0·1N-potassium hydroxide, gave no diffusion-current plateau but did give a decomposition voltage (E^*) at about $-1{\cdot}55$ v (versus S.C.E.), as found for tetrammineplatinum(II) chloride.[13] It, therefore, seems likely that in basic solution, when the nitrosyl complex has changed into the nitro-form, polarographic reduction to platinum metal takes place.

TABLE 2. *Polarographic reduction of* $[Pt(NO)(NH_3)_4Cl]Cl_2$ *at* 22° C.

(a) *Reduction with* 0·1N-KCl *as base electrolyte.*

Conc. of complex (mmole/l.)	1·3	0·60	0·32	0·15
i_d (in μA.)	6·0	2·7	1·5	0·70
$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	2·01	1·95	2·04	2·03
$E_{\frac{1}{2}}$ (*vs.* S.C.E.)	−1·06	−1·04	−1·04	−1·04

(b) *Reduction with* 0·1N-KOH *as base electrolyte.*

Conc. of complex (mmole/l.)	3·12	1·55	0·70	0·30	0·10
E^* (*vs.* S.C.E.)	−1·60	−1·58	−1·55	−1·50	−1·50

(d) *Potassium nitrosyltetranitronitratoplatinate*(II), $K_2[Pt(NO)(NO_2)_4(NO_3)]$. It has been reported [17] that potassium tetranitroplatinate(II) reacts with nitric acid to give $K_2[Pt(NO_2)_3(NO_3)_3]$, which is hydrolysed by water to $K_2[Pt(NO_2)_3(NO_3)_2(OH)]$.

It was found that potassium tetranitroplatinate(II) dissolved in concentrated nitric acid to give a deep blue solution from which no solid blue products could be isolated. The infrared spectrum of this solution showed a peak at 1750 cm.$^{-1}$. Evaporation of the blue solution on a steam-bath gave yellow crystals (which redissolved in water to give a yellow solution), $K_2[Pt(NO)(NO_2)_4NO_3)],2H_2O$. The complex was diamagnetic, and its infrared spectrum showed peaks typical of co-ordinated nitrato- and nitro-groups (see Table 3 and

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[13] Hall and Plowman, *Austral. J. Chem.*, 1956, **9**, 14.

[14] Zuman and Kabat, *Coll. Czech. Chem. Comm.*, 1954, **19**, 873.

[15] Lanza and Corbellini, *Contr. Tecr. e Sper. di Polarographia, Padova*, 1951, 133.

[16] Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.

[17] Tscherjajev and Hening, *Izvest. Inst. Isuceniju Platiny*, 1933, **11**, 46.

ref. 18) together with a peak at 1675 cm.$^{-1}$ attributed to a nitrosyl group. Conductivity measurements in water showed it to be a 2 : 1 electrolyte.

(e) *Miscellaneous platinum complexes.* Reactions of tetrammineplatinum(II) chloride in moderately concentrated nitric or acetic acids with nitric oxide gave the complexes $[Pt(NO)(NH_3)_4(OAc)]Cl_2$ and $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$. The infrared spectrum of the latter complex contains bands [18] typical of a co-ordinated nitrate group, and the given formulation is therefore preferred, although the formulation $[Pt(NO)(NH_3)_4Cl](NO_3)_2$ seems a possibility. It is difficult to be certain whether the acetate group is bound as a co-ordinated group.

According to Koefoed,[4] the complex $[Pt(NH_3)_2(NO_2)_2]$ reacts with hydrochloric acid to give $[Pt(NO)(NH_3)_2Cl]_{0\cdot75},H_2O$; and also $[Pt(NO)(NH_3)_4Cl]Cl_2$ reacts with sulphuric acid to give $[Pt(NO)(NH_3)_3(HSO_4)_{1\cdot5}(SO_4)_{0\cdot5}Cl_{0\cdot5}]$. Both these products were examined analytically and spectroscopically; neither gave nitro- or nitrosyl peaks in the infrared spectrum, and analyses showed the products to be respectively $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_4SO_4]Cl_2$. (The latter showed a peak at 1080 cm.$^{-1}$, attributed to an SO_4^{2-} group.)

(B) *Nitrosyl Complexes of Palladium.*—The only known palladium nitrosyl complexes are $[Pd(NO_2)Cl_2]$, $[Pd(NO)_2SO_4]$,[7,19] and $[Pd(NO)Cl]_n$.[20]

(a) *Potassium nitrosyltetranitronitratopalladate*(II), $K_2[Pd(NO)(NO_2)_4(NO_3)]$. This new compound was prepared in the same way as the analogous platinum complex by treating potassium tetranitropalladate(II) with nitric acid. The red crystalline product was diamagnetic and its infrared spectrum gave peaks in the co-ordinated nitro- and nitrato-regions, as well as a peak at 1720 cm.$^{-1}$. A comparison of the infrared spectra of known nitrosyl-nitro-nitrato-complexes shows several similarities (Table 3).

TABLE 3. *Infrared spectra of nitrosyl-nitro-nitrato-complexes.*

Complex	Frequencies (cm.$^{-1}$)							
$K_2[Pd(NO)(NO_2)_4(NO_3)]$	1720	1500	1300	1280	1010	995	800	790
$K_2[Pt(NO)(NO_2)_4(NO_3)]$	1675	1500	1350	1260	970	940	840	815
$[Ru(NO)(NO_2)_2(NO_3)(H_2O)_2]$ [21]	1931	1504	1300 [a]	1276	989	—	863, 833	786
Assignments made by Fletcher *et al.*[21]	NO	NO_3	—	NO_3	RuNO	—	NO_2	NO_3
Preferred assignments [b]	NO	NO_3	NO_2	NO_3	NO_3	NO_3	NO_2 or	NO_3

[a] Although Fletcher *et al.* list no peak at this frequency, the reproduction of the original spectrum in the paper clearly shows the presence of this band. [b] On the basis of the report by Gatehouse *et al.*[18] that co-ordinated nitrato-groups have bands near 1500, 1280, 1000, and 790 cm.$^{-1}$.

(b) *Other palladium nitrosyl complexes.* Although there was some evidence of a reaction between nitrosyl chloride in chloroform with $K_2[Pd(CN)_4]$ and $[Pd(NH_3)_4]Cl_2$, and of reaction between nitric oxide and a solution of tetramminepalladium(II) chloride in hydrochloric acid, no pure products could be isolated.

According to Manchot and Waldmüller,[19] nitric oxide and methanol vapour react with solid palladous nitrate to give palladous nitrite, $Pd(NO_2)_2$. This work was repeated by us. The black diamagnetic product gave two peaks in the infrared nitrosyl region (1810 and 1780 cm.$^{-1}$), together with peaks identical with those given by palladous nitrate. Analyses were variable, but the complex may be $[Pd^0(NO)_2(NO_3)_2]$, analogous to the dinitrosyl chloride and sulphate.[7,19]

(C) *Nitrosyl Complexes of Nickel.*—(a) *Nitrosyldi-amminehydroxynickel*(II) *hydroxide*, $[Ni(NO)(NH_3)_2OH](OH)_2$. It is reported [22] that a mixture of nitric oxide and ammonia gases reacts with nickel carbonyl in the presence of water to give the complex

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[18] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[19] Manchot and Waldmüller, *Ber.*, 1926, **59**, 2363.
[20] Schmidt and Jira, *Chem. Ber.*, 1960, **93**, 162.
[21] Fletcher, *Ricerca sci.*, 1958, **28** (Suppl.), 1.
[22] Frazer and Trout, *J. Amer. Chem. Soc.*, 1936, **58**, 2203.

$[Ni(NO)(NH_3)_5](NO_2)_2$. The preparation was repeated and a blue, amorphous product was obtained. The complex was paramagnetic with a moment of 2·9 B.M. at room temperatures, and the infrared spectrum showed bands at 3500 cm.$^{-1}$ (OH stretch), 1620 cm.$^{-1}$ (NH_3), and at 1780 cm.$^{-1}$ (NO). The analyses correspond to the formulation $[Ni(NO)(NH_3)_2(OH)](OH)_2$ or $[Ni(NO)(NH_3)_2(OH)_3]$. The blue colour[23] favours the former structure, in which case the complex is a direct analogue of $[Ni(NO)(OH)_3]$.[7] Although it has been pointed out that colour is in itself not diagnostic of tetrahedral nickel(II),[23] the extinction coefficients for $[Ni(NO)(OMe)_2(OH)]$ (at 650 mμ) and $[Ni(NO)(NH_3)(OMe)(OH)](OH)$ (see below) (at 637 mμ) were 99·1 and 56·0, respectively. These high values for ε are reasonable for a tetrahedral structure, and also by analogy the related compounds have been considered as tetrahedral.

(b) *Nitrosylamminehydroxymethoxynickel*(II) *hydroxide*, $[Ni(NO)(NH_3)(OMe)(OH)](OH)$. This new compound was prepared by passing a mixture of dry ammonia and nitric oxide into a methanolic solution of nickel carbonyl. It was blue and slightly soluble in water—in which it quickly decomposes—and in methanol. It was paramagnetic (see Table 4) with a moment of 3·14 B.M. and a θ of +27°, indicating that the nickel atom has two unpaired electrons.

TABLE 4. *Magnetic measurements on solid* $[Ni(NO)(NH_3)(OMe)(OH)(OH)$.

Temp. (°K)	295·6	271·0	258·0	231·5	214·0	184·0	163·5	137·0	118·0	103·0
$10^3\chi_A$ (c.g.s.u.)	3·63	4·13	4·32	4·76	5·29	5·94	6·50	7·25	8·58	9·48
$10^{-2}\chi_A^{-1}$	2·75	2·42	2·31	2·10	1·89	1·68	1·54	1·38	1·17	1·05

Diamagnetic correction for metal atom and ligands: -40×10^{-6} c.g.s.u.

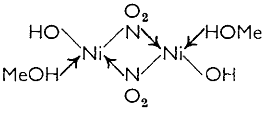
The infrared spectrum showed peaks in the OH stretching region (3500 cm.$^{-1}$), NH_3 region (1615 cm.$^{-1}$) and NO region (1785 cm.$^{-1}$) in addition to methanol peaks. The visible spectrum of a solution of the complex in methanol showed a peak at 637 mμ (ε 56). There was no evidence of isomerisation of the blue solid to a green nitro-compound as there was in the case of $[Ni(NO)(OH)(OMe)_2]$,[7] but a solution in methanol did isomerise to the green form (see below) when kept for longer than 24 hours. The ethanol and propanol complexes could not be obtained pure.

The structure which best accords with the spectral and magnetic data is

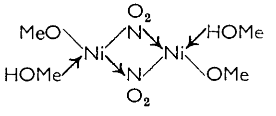
$$[Ni^{II}(NO)(NH_3)(OMe)(OH)](OH)$$

involving tetrahedral nickel.

(c) *Dimethanolate* μμ'*-dinitro-nickel*(II) *dihydroxide*, $[Ni(NO_2)(MeOH)_2(OH)]$. It was found that refluxing nitrosylamminehydroxymethoxynickel hydroxide in methanol gave a green insoluble product. The infrared spectrum showed the presence of OH and co-ordinated bridging NO_2 groups, as in $[Ni(NO_2)(MeOH)_2(OMe)]_x$.[7] There were no peaks in the nitrosyl region. The structure (I) is probably analogous to that of $[Ni(NO_2)(MeOH)_2(OMe)]_x$ (II):



(I)



(II)

and, in both cases, further polymerisation probably occurs through methoxy- or hydroxy-groups to give six-co-ordinate nickel.

(D) *The Co-ordinated* NO^- *Group*.—Since several of the metal complexes described in this paper could have been formulated with co-ordinated NO^-, we have considered it desirable to confirm the infrared criterion for detecting such a group: namely, a moderately strong band in the region 1045—1200 cm.$^{-1}$ which we have already discussed in connection with the red cobalt nitrosopentammines $[Co(NH_3)_5NO]X_2$ and $K_3[Co(CN)_5NO]$.[8,12] We

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[23] Katzin, *Nature*, 1958, **182**, 1013.

have assigned frequencies of 1045 and 1150 cm.$^{-1}$, respectively, to the stretching mode of the NO$^-$ ligand in [Co(NH$_3$)$_5$NO](NO$_3$)$_2$ and K$_3$[Co(CN)$_5$NO].[12] However, in a recent study of amminecobalt complexes, including the red nitrosopentammines, by Quagliano and his colleagues [26] it was suggested that N–H vibrations were responsible for these frequencies and that the N–O stretching vibration was at 1620 cm.$^{-1}$. Whilst in our opinion the occurrence of absorption at *ca.* 1100 cm.$^{-1}$ by other complexes not containing ammonia, *e.g.*, K$_3$[Co(CN)$_5$NO] and [Fe(NO)$_3$NO],[12,32] is clear evidence for a stretching frequency associated with the NO$^-$ group, we have felt it necessary to confirm our original assignment in the ammine and cyano-salts by using isotopic substitution of the NO group. The observed and the calculated frequencies are recorded in Table 5. The proportion of ^{15}NO in the nitric oxide was estimated by infrared spectroscopy as 61 ± 5% of the total.

TABLE 5. *Infrared spectra (in cm.$^{-1}$) in* NO$^-$ *complexes with isotopic replacement.*

Complex	[Co(NH$_3$)$_5$NO](NO$_3$)$_2$	K$_3$[Co(CN)$_5$NO]
Strong bands in ^{14}NO complex	1610, 1300, 1045, 930, 820	2141, 2104sh, 1150
Strong bands in ^{15}N-enriched complex...	1610, 1300, 1045, 1017, 930, 820	2141, 2104sh, 1150, 1119
Separation of NO– bands	28	31
Calculated separation of NO$^-$ bands [higher frequency $(1 - \sqrt{14/15})$]	27	30
Ratio of intensities of peak in doublet (^{15}NO/total) (as %)	56 ± 5	58 ± 5

It is thus clear that the bands in the 1100 cm.$^{-1}$ region in the red nitrosopentammines and in the cyanide complex arise from the NO$^-$ group and not from ammine deformation frequencies. The band at 1620 cm.$^{-1}$ assigned by Quagliano and his colleagues to the N–O stretch did not shift in the enriched compounds, and must clearly be an N–H bending mode.

We finally note, in connexion with the cobalt complexes, that aqueous solutions of the red nitrate and of the nitrosyl cyanide have conductivities indicating that they are respectively 2 : 1 and 3 : 1 complexes. (Molar conductivities in water = 251 and 344 ohm^{-1} cm.^{2}, respectively.)

EXPERIMENTAL

Microanalyses and molecular weights are by the Microanalytical Laboratory, Imperial College.

Potassium Nitrosylpentachloroplatinate(II), K$_2$[Pt(NO)Cl$_5$].—A suspension of potassium chloroplatinate(II) (2 g.) was shaken with a saturated solution of nitrosyl chloride in anhydrous chloroform (200 ml.) for 24 hr. The green unstable *complex* (2 g., 95%) was removed by filtration and dried *in vacuo* {Found: K, 16·0; N, 2·8; Cl, 37·5. K$_2$[Pt(NO)Cl$_5$] requires K, 16·25; N, 2·9; Cl, 36·8%}.

Tetramminenitrosylchloroplatinum(II) *Dichloride*, [Pt(NO)(NH$_3$)$_4$Cl]Cl$_2$.—(*a*) This complex was prepared by Jensen's method [3] from tetrammineplatinum(II) chloride in hydrochloric acid solution with nitric oxide {Found: Pt, 48·5; Cl, 26·3; N, 17·2. Calc. for [Pt(NO)(NH$_3$)$_4$Cl]Cl$_2$: Pt, 48·8; Cl, 26·6; N, 17·5%}. Molar conductivity in water = 294 ohm^{-1} cm.^{2}.

(*b*) Tetrammineplatinum(II) chloride (2 g.) was suspended in a saturated solution of nitrosyl chloride in chloroform (200 ml.) and shaken for 24 hr. The green, stable solid was removed by filtration and dried *in vacuo* (yield 2 g., 95%) (Found: Pt, 48·3; N, 17·7; Cl, 26·5%).

Nitrosylbis(ethylenediamine)chloroplatinum(II) *Dichloride*, [Pt(NO)en$_2$Cl]Cl$_2$.—This salt was prepared as above, but from bis(ethylenediamine)platinum(II) chloride (2 g.). It was green and could not be obtained pure (yield, 2 g., 95%) {Found: C, 10·9; H, 3·2; N, 20·1. Calc. for [Pt(NO)en$_2$Cl]Cl$_2$: C, 12·2; H, 4·0; N, 21·3%}.

Potassium Nitrosyltetranitrochloroplatinate(II), K$_2$[Pt(NO)(NO$_2$)$_4$Cl].—Potassium tetranitroplatinate(II) (2 g.) was shaken with a saturated solution of nitrosyl chloride in chloroform (200 ml.) for 24 hr. The *product* (2 g., 95%) was green {Found: K, 15·3; Pt, 37·4; N, 13·4. K$_2$[Pt(NO)(NO$_2$)$_4$Cl] requires K, 15·0; Pt, 37·3; N, 14·3%}.

Dipyridinonitrochloroplatinum(II), [Pt py$_2$(NO$_2$)Cl].—Potassium chloroplatinate(II) (2 g.) in water (20 ml.) was shaken for 24 hr. in a slow current of nitric oxide, and pyridine was then added in excess. The yellow precipitate was filtered off, washed with water, alcohol, and ether, and dried *in vacuo* (yield, 1·5 g., 75%) {Found: Pt, 44·5; N, 9·6; Cl, 27·6; H, 2·4. Calc. for $[Ptpy_2(NO_2)Cl]$: Pt, 44·9; N, 9·7; C, 27·6; H, 2·3%}.

Pyridinium Chloroplatinate(II), $(pyH)_2[PtCl_4],4H_2O$.—The complex $[Pt\,py_2(NO_2)Cl]$ (1 g.) was heated for 4 hr. with 17% hydrochloric acid on the steam-bath. The yellow crystalline product was filtered off, washed with water and alcohol, and dried *in vacuo* {Found: Pt, 34·5; C, 21·6; N, 5·3. Calc. for $(pyH)_2[PtCl_4],4H_2O$: Pt, 34·6; C, 21·9; N, 5·1%}.

Nitrosyltetrammineacetatoplatinum(II) *Chloride*, $[Pt(NO)(NH_3)_4OAc]Cl_2$.—Tetrammineplatinum(II) chloride (2 g.) was dissolved in 50% acetic acid (70 ml.) and kept saturated with nitric oxide for 4 hr. The green solid *complex* was filtered off and washed with water, alcohol, and ether (yield, 0·7 g., 30%) {Found: Pt, 42·7; C, 4·7; H, 3·7. $[Pt(NO)(NH_3)_4OAc]Cl_2$ requires Pt, 42·4; C, 5·2; H, 3·8%}.

Nitrosyltetramminenitratoplatinum(II) *Nitrate Chloride*, $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$.—Tetrammineplatinum(II) chloride (2 g.) was dissolved in 8N-nitric acid (80 ml.) and kept saturated with nitric oxide for 6 hr. The bright green solid *complex* (0·5 g., 20%) was filtered off and washed with alcohol and ether, and dried *in vacuo* {Found: Pt, 43·5; Cl, 8·6; N, 21·6. $[Pt(NO)(NH_3)_4(NO_3)](NO_3)Cl$ requires Pt, 44·1; Cl, 7·9; N, 21·7%}.

Potassium Nitrosyltetranitronitratoplatinate(II), $K_2[Pt(NO)(NO_2)_4(NO_3)],2H_2O$.—Potassiumtetranitroplatinate(II) (2 g.), was treated with 8N-nitric acid (80 ml.), and the blue solution heated for 4 hr. on the steam-bath. The yellow residue of *complex* (0·6 g., 25%) was recrystallised from 0·1N-nitric acid {Found: K, 13·7; Pt, 33·5; N, 13·1. $K_2[Pt(NO)(NO_2)_4(NO_3)],2H_2O$ requires K, 13·1; Pt, 33·4; N, 13·9%}. Molar conductivity in water = 252 ohm^{-1} $cm.^2$.

Diammineplatinum(IV) *Tetrachloride*, $[Pt(NH_3)_2Cl_4],H_2O$.—Diammineplatinum(II) dinitrite (1 g.) was treated with an excess of 6N-hydrochloric acid for 2 hr. at 80°. The yellow precipitate (0·5 g., 45%) was filtered off, washed with water, alcohol, and ether, and dried *in vacuo* {Found: Pt, 50·7; Cl, 37·1. Calc. for $[Pt(NH_3)_2Cl_4],H_2O$: Pt, 50·2; Cl, 36·5%}.

Tetramminesulphatoplatinum(IV) *Dichloride*, $[Pt(NH_3)_4SO_4]Cl_2$.—Nitrosyltetramminechloroplatinum(II) chloride (2 g.) was treated with 50% sulphuric acid (50 ml.) at 90° for 3 hr. Bright red crystals of the *complex*, which was sparingly soluble in water, were filtered off, washed with water, alcohol, and ether, and dried *in vacuo* (yield, 1 g., 40%) {Found: Pt, 40·5; N, 11·2. $[Pt(NH_3)_4SO_4]Cl_2$ requires Pt, 40·7; N, 11·7}.

Potassium Nitrosyltetranitronitratopalladate(II), $K_2[Pd(NO)(NO_2)_4(NO_3)],2H_2O$.—Potassium tetranitropalladate (2 g.) was treated with 8N-nitric acid at 80° for 2 hr. The red *product* (1 g., 25%) was recrystallised from 0·1N-nitric acid {Found: K, 15·5; Pd, 22·5; N, 16·1. $K_2[Pd(NO)(NO_2)_4(NO_3)],2H_2O$ requires K, 15·5; Pd, 22·0; N, 16·7%}.

Nitrosyldiamminehydroxynickel(II) *Dihydroxide*, $[Ni(NO)(NH_3)_2(OH)](OH)_2$.—A mixture of ammonia and nitric oxide gases (supplied from cylinders and dried) was passed into a solution of nickel carbonyl (5 ml.) in ether (100 ml.) for 3 hr. The blue solid complex (0·5 g., 10%) thus formed was filtered off, washed, and dried *in vacuo* {Found: Ni, 32·2; N, 23·7. Calc. for $[Ni(NO)(NH_3)_2(OH)](OH)_2$: Ni, 33·8; N, 24·2%}. $\chi_A = 3{\cdot}08 \times 10^{-3}$ c.g.s.u. at 295° K.

Nitrosylamminehydroxymethoxynickel(II) *Hydroxide*, $[Ni(NO)(NH_3)(OMe)(OH)](OH)$.—A mixture of ammonia and nitric oxide gases was passed into a solution of nickel carbonyl (5 ml.) in methanol (120 ml.) for 3 hr. The blue *product* (0·5 g., 9%) crystallised from methanol {Found: C, 7·7; H, 3·9; N, 15·7. $[Ni(NO)(NH_3)(OMe)(OH)](OH)$ requires C, 7·1; H, 4·7; N, 16·4%}.

$\mu\mu'$-Dinitrodimethanolatedinickel(II) *Dihydroxide*, $[Ni(NO_2)(OH)(MeOH)]_2,2H_2O$.—The above described nitrosyl complex (2 g.) was refluxed for 6 hr. with 97% methanol under nitrogen. The green, insoluble *product* (1·8 g., 90%) was filtered off, washed with methanol and alcohol, and dried *in vacuo* {Found: C, 7·3; H, 3·9; N, 7·4. $[Ni(NO_2)(OH)(MeOH)]_2,2H_2O$ requires C, 7·0; H, 4·1; N, 8·1%}.

Other Preparations.—The complexes $[Co(NH_3)_5NO](NO_3)_2$ and $K_3[Co(CN)_5NO]$ were made in the known manner.[12] $[^{15}N]$Nitric oxide was obtained by warming a mixture of enriched potassium nitrite with potassium iodide and sulphuric acid.[29]

Potassium tetranitroplatinate(II) and tetranitropalladate(II) were made by the recorded methods,[25,28] as were tetrammineplatinum(II) chloride and di(ethylenediamine)platinum(II)

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chloride.[30] Nitrosyl chloride was prepared from nitrosylsulphuric acid and sodium chloride, and was purified by redistillation.[31]

Physical Measurements.—Infrared spectra were measured on a Perkin–Elmer recording spectrophotometer, model 21, with sodium chloride optics; absorption spectra were measured on a Perkin–Elmer Spectracord, model 4000, with 1-cm. silica cells.

Polarographic measurements were made with a Tinsley model 19 recording instrument ($m^{\frac{2}{3}}t^{\frac{1}{6}} = 2{\cdot}3$); magnetic measurements at room temperatures were made by the Gouy method with a permanent field of 6500 gauss; those over a temperature range were measured at a field of 5100 gauss.

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