179. *Infrared Spectra of Transition Metal–Nitric Oxide Complexes. Part IV.* The Pentacyanonitrosyl-complexes of Chromium and Molybdenum.*

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Infrared, polarographic, and magnetic-susceptibility measurements have been made on the new compound $K_3[Cr^I(CN)_5NO],H_2O$. On the basis of infrared spectral and other evidence we reformulate the previously reported $K_4[Mo^0(CN)_5NO],2H_2O$ as an octaco-ordinated bivalent molybdenum complex, $K_4[Mo^{II}(OH)_2(CN)_5(NO)]$; a known hydroxycyanomolybdate is also reformulated as $K_3[Mo^V(OH)_4(CN)_4],2H_2O$.

The use of hydroxylamine for the introduction of a nitrosyl group into transition-metal cyanide complexes has been known for some time.[1,2] A cyanomononitrosylchromium complex has been prepared by using conditions similar to those for the preparation of a molybdenum complex,[2] which was formulated as $K_4[Mo(CN)_5NO],2H_2O$. Whilst the chromium complex has an anion of stoicheiometry reported for this molybdenum compound, *i.e.* it is $K_3[Cr^I(CN)_5NO],H_2O$, infrared and other measurements lead us to reformulate the molybdenum complex with the metal atom having octaco-ordination, *i.e.* as $K_4[Mo^{II}(OH)_2(CN)_5(NO)]$.

Potassium pentacyanonitrosylchromate(I) *monohydrate,* $K_3[Cr(CN)_5NO],H_2O$. This compound was obtained by treating chromium trioxide in basic solution containing excess of cyanide ion with hydroxylamine. The bright green complex is very stable as a solid and in aqueous solution.

Magnetic-susceptibility measurements were made on the solid over a temperature range (Table 1); a plot of $1/\chi_A$ against T is linear and the calculated moment is 1·87 B.M.,

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* Part III, *J.*, 1958, 3993.

[1] Hieber and Nast, *Z. anorg. Chem.*, 1940, **244**, 23; Hieber and Nast, *FIAT Review of German Science*, 1939—46, *Inorg. Chem.*, Part II, p. 146.

[2] Nast and Gehring, *Z. anorg. Chem.*, 1948, **256**, 169.

with a value of θ of —7°. The complex clearly has a single unpaired electron, in agreement with its formulation as a chromium(I) complex.

TABLE 1. *Magnetic susceptibility of solid* $K_3[Cr(CN)_5NO],H_2O$.

$T°$ (K)	295·6	265·0	230·0	198·0	158·0	124·0	85·0
$\chi_A \times 10^3$ (c.g.s.u.)	1·44	1·57	1·84	2·11	2·61	3·23	4·93
$1/\chi_A \times 10^2$ (c.g.s.u.)	6·95	6·35	5·45	4·75	3·83	3·10	2·03

Diamagnetic corrections were taken as -160×10^{-6} c.g.s.u.

There is an intense peak in the infrared spectrum (Table 2) at 1625 cm.$^{-1}$, which is quite different in appearance from that of H–O–H bending vibrations that also occur in this region, and is clearly assignable to an N–O stretching frequency. In the C–N stretching region there is a strong peak at 2137 cm.$^{-1}$ with a shoulder at 2095 cm.$^{-1}$, a structure found previously [3] in other complexes, *e.g.* $K_3[Co(CN)_5NO]$.

Polarographic reduction of a 0·01M-solution of the complex in aqueous 1M-potassium cyanide showed a well-defined wave corresponding to a one-electron reversible reduction. The half-wave potential was —0·93 v versus the standard mercurous chloride electrode. The product of the reduction must be $K_4[Cr^0(CN)_5NO]$, but attempts to isolate it have failed.

It is noteworthy that for the complexes $[M(CN)_5NO]$, the stability order is Fe(III) < Mn(II) < Cr(I); thus the iron complex exists only in solution and the manganese complex is very unstable. If we assume, with Pauling, that the bonds in this complex have about 50% covalent character, the formation of six such bonds would lead to resultant charges of —2, —1, and 0 for the chromium, manganese, and iron complexes, respectively. The negative charge is dissipated, in agreement with Pauling's electroneutrality principle, by

TABLE 2. *Infrared spectra* (*cm.*$^{-1}$) *of chromium and molybdenum complexes.*

$K_3[Cr(CN)_5NO],H_2O$	$\underset{\text{CN str}}{\text{2137vs,}}\ \underset{\text{CN str}}{\text{2095sh,}}\ \underset{\text{NO str}}{\text{1645vs}}$
$K_4[Mo(OH)_2(CN)_5NO]$	$\underset{\text{OH str}}{\text{3300—3500,}}\ \underbrace{\text{2130s, 2106s, 2081vs, 2062vs, 2037vs,}}_{\text{CN str}}\ \underset{\text{NO str}}{\text{1595vs,}}\ \underbrace{\text{980m, 835b,}}_{\text{MoO str?}}$ 580m, 475m, 375w
$K_4[Mo(OH)_4(CN)_4]$	$\underset{\text{OH str}}{\text{3300—3500,}}\ \underbrace{\text{2105s, 2083vs, 2055w, sh,}}_{\text{CN str}}\ \underbrace{\text{925w, 825b}}_{\text{MoO str?}}$
$K_3[Mo(OH)_4(CN)_4],2H_2O$	$\underset{\text{OH str}}{\text{3300—3500,}}\ \underbrace{\text{2100s, 2080vs, 2055s,}}_{\text{CN str}}\ \underbrace{\text{925m, 825b}}_{\text{MoO str?}}$
$K_4[Mo(OH)_3(CN)_5],nH_2O$	$\underset{\text{OH str}}{\text{3300—3500,}}\ \underbrace{\text{2106vs, 2058vs,}}_{\text{CN str}}\ \underbrace{\text{920m, 840sb}}_{\text{MoO str?}}$
$K_4[Mo(CN)_8],2H_2O$ * [a]	2118vs, 2096vs, 2050vs
$K_3[Mo(CN)_8],2H_2O$ * [a]	2118vs, 2096vs, 2045vs
$Na_2MoO_4,2H_2O$ [b]	$\underbrace{\text{900m, 855m, 820s, b}}_{\text{MoO str}}$
$K_2MoO_4,5H_2O$ [14]	$\underbrace{\text{900m, 825s, b}}_{\text{MoO str}}$

* CN stretching region only is quoted.

† Absorption in 800—1000 cm.$^{-1}$ region only quoted; $PbMoO_4$ also absorbs in this region.

[a] Brane, Johnson, Larsen, and Meloche, *J. Inorg. Nuclear Chem.*, 1958, **6**, 99.

[b] Miller and Wilkins, *Analyt. Chem.*, 1951, **24**, 1253.

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

the formation of π-bonds between the metal and the ligands. Thus the maximum π-bonding and stability would occur for chromium; the N–O stretching frequency accordingly decreases in the same order as the increased metal–ligand double bonding.

Potassium dihydroxopentacyanonitrosylmolybdate(II), $K_4[Mo^{II}(OH)_2(CN)_5(NO)]$. This compound was first prepared, but wrongly formulated, by Hofmann;[4] later Nast and Gehring,[2] after extensive analyses, ascribed to it the formula $K_4[Mo^0(CN)_5NO],2H_2O$. We have examined the infrared spectra of this compound and those of some other hydroxy-cyano-complexes of molybdenum (Table 2). The main features of the spectrum of the compound are: (*a*) Strong absorption maxima in the region 3300—3500 cm.$^{-1}$, indicative of hydroxy-groups. Similar absorptions are found in the spectra of the other hydroxycyano-molybdenum complexes which, on other grounds, must be formulated as having hydroxy-groups bound to the metal atom. (*b*) In the region 2040—2200 cm.$^{-1}$ there is a rather complex splitting of cyanide group frequencies. The positions of the main peaks are comparable to those found for the hydroxycyano-complexes, but the degree of splitting is much greater. This can be attributed partly to the greater asymmetry introduced by the nitric oxide ligand and also to different crystalline lattice effects. (*c*) There is very weak and diffuse absorption at 1620 cm.$^{-1}$ which can be attributed to traces of water in the mulls. (*d*) At 1595 cm.$^{-1}$ there is an intense absorption which we assign as an N–O stretching frequency of the bound NO^+ group. Hieber and Jahn [5] have recently claimed that a peak at 1410 cm.$^{-1}$ should be assigned to the N–O stretching frequency. We have examined this region in both Nujol and hexachlorobutadiene mulls and consider that this very weak absorption is more likely to arise from a combination mode, especially because of its low intensity and the fact that absorption by an NO^+ group at such a low frequency is very unlikely (as suggested by experience with a large number of other nitric oxide complexes [6]). The frequency of the N–O stretching in this molybdenum compound and in the chromium compound discussed above is very low and occurs at the extreme end of the scale for NO^+ co-ordination.[3,6] The low value can in part be explained by the donation of electron density from the π-bonds of the nitric oxide group to the metal atom as suggested by Alderman and Owston [7] to explain the non-linearity of the M–N–O system in cobalt nitrosyl dithiocarbamate. (*e*) There are broad and strong peaks in the region 800—950 cm.$^{-1}$ which also occur in the hydroxycyano-compounds and in sodium, potassium, and lead molybdates (Table 2); these bands are not present in $K_3[Mo(CN)_8]$ or in $K_4[Mo(CN)_8]$ or in normal, sexaco-ordinate cyanonitrosyl-complexes.[3,6,8] It seems most likely that these absorptions are attributable to Mo–O stretching modes.

In addition to this spectral evidence, chemical and magnetic-susceptibility data also support the new formulation. Thus the complex does not lose water at 180° even under vacuum,[2] a fact we have confirmed. Magnetic-susceptibility measurements at room temperature show a slight paramagnetism ($\chi_g = +0{\cdot}36 \times 10^{-6}$ c.g.s.u.) which corresponds to considerably less than the moment for one unpaired spin. The complex is therefore diamagnetic, the first example, so far as we are aware, of such a state for Mo(II) in a dodecahedron. Recent theoretical work [9] indicates that octaco-ordinate Mo(II) complexes would be diamagnetic as the 4*d* orbitals are split into three singlets and a doublet level, under the influence of the ligand field for a dodecahedron arrangement.

The formulation of the nitrosyl as $K_4[Mo^{II}(OH)_2(CN)_5(NO)]$ suggested that other molybdenum species could be similarly reformulated. Thus the complex hydroxy-cyanide first prepared by von der Steide and Hofmann [4] was considered by Bucknall and Wardlaw [10] to be $K_3[Mo^{IV}(OH)_3(CN)_4H_2O],2H_2O$. We have studied its infrared spectrum

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[4] von der Steide and Hofmann, *Z. anorg. Chem.*, 1896, **12**, 282.
[5] Hieber and Jahn, *Z. Naturforsch.*, 1958, **13b**, 196.
[6] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[7] Alderman and Owston, *Nature*, 1956, **178**, 1071.
[8] Herington and Kynaston, *J.*, 1955, 3555.
[9] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.
[10] Bucknall and Wardlaw, *J.*, 1927, 2981.

(Table 2) and found that its magnetic susceptibility corresponds to a moment of 1·91 B.M. It therefore appears that the complex is derived from Mo(V) and is best formulated as $K_3[Mo^{V}(OH)_4(CN)_4],2H_2O$. An alternative formulation of the hydroxy-complex species with Mo=O bonds, *e.g.*, $K_3[Mo^{III}O_2(CN)_4(H_2O)_2],2H_2O$, is also possible and would be consistent with the properties.

EXPERIMENTAL

Infrared measurements were made with a Perkin-Elmer Model 21 recording spectrophotometer with calcium fluoride, sodium chloride, and potassium bromide optics for the appropriate regions. The spectra were taken in Nujol or hexachlorobutadiene mulls. Magnetic measurements were made by the standard Gouy technique on finely ground solids. Polarograms were taken on a Tinsley recording instrument, Type 19/1.

Potassium Pentacyanonitrosylchromate(I) *Hydrate*.—Chromium trioxide (7 g.) was added to a cold saturated solution of potassium hydroxide (20 g.) with ice cooling. Saturated aqueous potassium cyanide (35 g.) was then added and the mixture filtered. Hydroxylamine hydrochloride (8 g.) was added to the filtrate and the solution was heated (steam-bath) for 2 hr., and then filtered and cooled, and the filtrate poured, with stirring, into ethanol (95%; 250 ml.). The precipitate was dissolved in the minimum quantity of water, and the compound again precipitated with ethanol; two crystallisations from water gave large bright green crystals (5 g., 20%) (Found: K, 33·6; Cr, 14·9; C, 18·05; N, 24·3; H_2O, 5·1. $K_3[Cr(CN)_5NO],H_2O$ requires K, 33·8; Cr, 15·0; C, 17·3; N, 24·2; H_2O, 5·2%).

The water of crystallisation was removed at 80° *in vacuo* to give the anhydrous complex.

Potassium Dihydroxypentacyanonitrosylmolybdate(II).—This was prepared by the literature method[2] (Found: K, 35·5; C, 13·1. Calc. for $K_4[Mo(OH)_2(CN)_5NO]$: K, 34·9; C, 13·45%). Potassium tetrahydroxotetracyanomolybdate(V) was obtained as described earlier[10] (Found: K, 27·3; Mo, 22·8. Calc. for $K_3[Mo(CN)_4(OH)_4],2H_2O$: K, 27·8; Mo, 22·7%). The complexes $K_4[Mo(CN)_4(OH)_4]$ [4,10,11] and $K_4[Mo(CN)_5(OH)_3]$ [12] were prepared by published methods.

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[11] Péchard, *Compt. rend.*, 1894, **118**, 804.

[12] Collenberg, *Z. anorg. Chem.*, 1924, **136**, 249.