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# Hydroxylamine Complexes of Chromium. The Crystal Structure of Diaquanitrosyl(pyridine-2,6-dicarboxylato)chromium

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The reaction of chromium(VI) with excess hydroxylamine has in the past been used to generate complexes containing the $\{Cr(NO)\}^{2+}$ moiety [1–6]. Complexes of chromium containing hydroxylamine or hydroxylamido (1–) ligands have not been characterized previously.

We found that aqueous solutions of $CrO_4{}^{2-}$ in the presence of dipicolinic acid (pyridine-2,6-dicarboxylate = dipic) react with $[NH_3OH]Cl$ at pH 4–5 to yield three different products: $[Cr(dipic)(NO)(H_2O)_2]$ (I, red), $[Cr(dipic)(NO)(H_2NOH)_2]\cdot 3H_2O$ (II, yellow-green) and $[Cr(dipic)(H_2NO)(H_2NOH)_2]$ (III, dark green). The complexes I and II show effective magnetic moments of 1.70 $\mu_B$ and 1.71 $\mu_B$ at 298 K, respectively, in agreement with complexes of the type $\{Cr{-}NO\}^5$ with one unpaired electron. III has an effective magnetic moment of 3.6 $\mu_B$ (298 K) indicating a $d^3$ configuration of Cr(III). In the infrared spectra of I and II $\nu(NO)$ frequencies at 1725 and 1710 $cm^{-1}$, respectively, are observed; $\nu(C{=}O)$ and $\nu(C{-}O)$ bands at 1630 and 1350 $cm^{-1}$ indicate coordinated carboxylato groups of the dipic ligands for **I**, **II** and **III**. It is at present not possible to unambiguously assign the mode of coordination of neutral hydroxylamine ligands in **II** and **III**. Normal N-coordination of $H_2NOH$ or O-coordination of $O{-}NH_3$ are conceivable. The hydroxylamido(1–) ligand is most probably O,N-coordinated [10]. The complex $[Cr(dipic)NO(H_2O)_2]$ crystallizes in the rhombic system, space group $D_{2h}{}^{14}$ – *Pcnb* with cell dimensions $a$ = 9.245(3), $b$ = 9.745(2), $c$ = 11.186(2) Å and $Z$ = 4.

Intensity data were collected on an AED (Siemens) diffractometer using Mo-$K_\alpha$ radiation with a $\theta{-}2\theta$ scan technique ($2\theta \leqslant 60°$). The structure was solved by Patterson and Fourier syntheses. 1109 independent reflections ($I \geqslant 3\sigma(I)$) were refined by

TABLE I. Final Positional Parameters and Anisotropic Thermal Parameters for $[Cr(dipic)(NO)(H_2O)_2]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr | 0.0 | 0.25 | 0.05034(6) | 0.0250(3) | 0.0185(3) | 0.0172(3) | 0.0 | 0.0 | 0.0010(3) |
| O1 | 0.2519(4) | 0.5162(3) | 0.2343(2) | 0.052(2) | 0.046(2) | 0.031(1) | 0.0005(12) | −0.005(1) | −0.025(1) |
| O2 | 0.1367(2) | 0.4062(2) | 0.0898(2) | 0.033(1) | 0.023(1) | 0.022(1) | 0.002(1) | 0.0017(9) | −0.04(1) |
| O3 | 0.1686(3) | 0.1203(3) | 0.0587(2) | 0.033(1) | 0.028(1) | 0.025(1) | −0.003(1) | −0.004(1) | 0.009(1) |
| O4 | 0.0 | 0.25 | −0.2073(4) | 0.094(4) | 0.094(4) | 0.022(2) | 0.0 | 0.0 | 0.021(4) |
| N1 | 0.0 | 0.25 | 0.2302(3) | 0.024(2) | 0.019(1) | 0.020(1) | 0.0 | 0.0 | −0.0002(20) |
| N2 | 0.0 | 0.25 | −0.1016(3) | 0.038(2) | 0.031(2) | 0.021(2) | 0.0 | 0.0 | 0.008(2) |
| C1 | 0.1653(4) | 0.4292(3) | 0.2011(3) | 0.032(2) | 0.026(1) | 0.025(1) | 0.0005(12) | 0.0007(12) | −0.002(1) |
| C2 | 0.0837(4) | 0.3398(3) | 0.2870(3) | 0.026(1) | 0.027(1) | 0.023(1) | 0.00(1) | −0.0009(12) | −0.004(1) |
| C3 | 0.0859(4) | 0.3419(4) | 0.4105(3) | 0.034(2) | 0.051(2) | 0.024(2) | −0.002(1) | −0.002(1) | −0.015(2) |
| C4 | 0.0 | 0.25 | 0.4718(4) | 0.043(3) | 0.060(3) | 0.017(2) | 0.0 | 0.0 | −0.012(3) |
| H1 | 0.198(5) | 0.091(5) | 0.116(4) | 0.05(1)[a] | | | | | |
| H2 | 0.166(5) | 0.062(5) | 0.013(4) | 0.05(1) | | | | | |
| H3 | 0.1460(4) | 0.4059(4) | 0.4528(3) | 0.06(1) | | | | | |
| H4 | 0.0 | 0.25 | 0.5576(4) | 0.06(1) | | | | | |

[a] Isotropic temperature factor. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

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TABLE II. Bond Distances [Å] and Angles [°].

| | | | | | |
|---|---|---|---|---|---|
| Cr–O2 | 2.027(2) | O4–N2–Cr | 180.0 | C1–O2–Cr | 117.9(2) |
| Cr–N2 | 1.699(4) | N2–Cr–O2 | 102.6(1) | C2–C1–O2 | 114.4(3) |
| Cr–N1 | 2.012(3) | N1–Cr–O2 | 77.4(1) | O1–C1–O2 | 123.2(3) |
| Cr–O3 | 2.009(3) | N1–Cr–N2 | 180.0 | O1–C1–C2 | 122.5(3) |
| N2–O4 | 1.182(5) | O3–Cr–O2 | 88.8(1) | C1–C2–N1 | 111.7(3) |
| O3–H1 | 0.76(5) | O3–Cr–N2 | 92.7(1) | C3–C2–N1 | 119.7(3) |
| O3–H2 | 0.76(5) | O3–Cr–N1 | 87.3(1) | C3–C2–C1 | 128.6(3) |
| N1–C2 | 1.329(4) | O2′–Cr–O2 | 154.8(1) | C2–C3–C4 | 118.6(3) |
| C1–O2 | 1.292(4) | O2′–Cr–N2 | 102.6(1) | C3–C4–C3′ | 120.4(4) |
| C1–C2 | 1.501(5) | O2′–Cr–N1 | 77.4(1) | C2–N1–Cr | 118.5(2) |
| C1–O1 | 1.223(5) | O2′–Cr–O3 | 90.1(1) | C2–N1–C2′ | 122.9(4) |
| C2–C3 | 1.382(5) | O3′–Cr–O2 | 90.1(1) | H1–O3–Cr | 124(4) |
| C3–C4 | 1.379(4) | O3′–Cr–N2 | 92.7(1) | H2–O3–Cr | 114(4) |
| | | O3′–Cr–N1 | 87.3(1) | H2–O3–H1 | 108(5) |
| | | O3′–Cr–O3 | 174.7(1) | | |
| | | O3′–Cr–O2′ | 88.8(1) | | |

least squares procedures to a final $R$ of 0.046 with anisotropic thermal parameters for all non-hydrogen atoms and an isotropic parameter $U = 0.06$ for all hydrogen atoms. The positions of all hydrogen atoms were located from a difference Fourier synthesis. Final atomic coordinates are given in Table I; bond distances and bond angles are summarized in Table II.

The overall symmetry of the neutral molecule is $C_2$; there is a two-fold rotation axis through the atoms O4, N2, Cr, N1, C4, H4 (Fig. 1). The tridentate pyridine-2,6-dicarboxylato ligand is coordinated to the chromium center; the bond distances and angles are very similar to those observed in $[Cr(dipic)(OH)(H_2O)]_2$ [7]. The nitrosyl group is bound in a *trans*-position with respect to the pyridine nitrogen; the Cr–N2 bond distance of 1.699(4) Å indicates considerable double bond character. The Cr–NO moiety is linear, the Cr–N and N–O distances agree well with those observed in $[Co(en)_3][Cr(NO)(CN)_5]$ [8] and in $[Cr(NO)(NO_2)_2(Pyr)_3]$ [9].

## Experimental

### *$[Cr(dipic)(NO)(H_2NOH)_2]\cdot 3H_2O$*

1.5 g of $Na_2Cr_2O_7$ and 1.9 g of pyridine-2,6-dicarboxylic acid were dissolved in 80 ml of water and the pH was adjusted to 12 by addition of 1 M NaOH. Solid $[H_3NOH]Cl$ was added in large excess until the pH of the solution dropped to 4.5. A grey solid precipitated ($Cr(OH)_3$?). The temperature was raised to 70 °C for 5 minutes until a clear solution was obtained. Upon cooling yellow-green crystals precipitated; they were filtered off, washed with ethanol and ether and air dried.

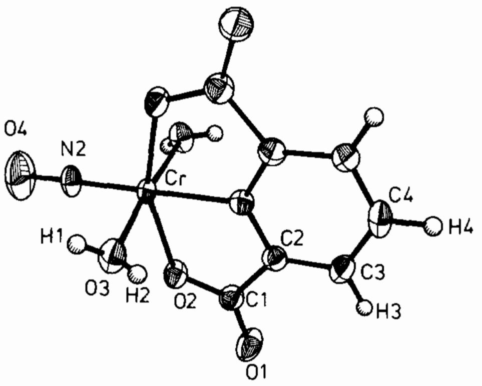

Fig. 1. The crystal structure of diaquanitrosyl(pyridine-2,6-dicarboxylato)chromium.

### *$[Cr(dipic)(H_2NO)(H_2NOH)_2]$*

This complex was prepared following the above procedure at higher concentrations of the reactants (3 g $Na_2Cr_2O_7$, 4 g pyridine-2,6-carboxylic acid in 80 ml of water). After cooling and removal of crystalline $[Cr(dipic)(NO)(H_2NOH)_2]\cdot 3H_2O$ the filtrate was allowed to stand at room temperature for 3 days after which time dark green crystals of $[Cr(dipic)(H_2NO)(H_2NOH)_2]$ were filtered off.

### *$[Cr(dipic)(NO)(H_2O)_2]$*

The above solutions were acidified after the reaction with hydroxylamine had been completed with conc. HCl (pH 0.5) and were allowed to stand in an open vessel for two weeks: red crystals of $[Cr(dipic)(NO)(H_2O)_2]$ were obtained.

Elemental analyses (C, H, N, Cr) of all complexes gave satisfactory values.

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