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Contribution from the Department of Chemistry,
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Synthesis and Molecular Structure of a Nitridochromium(V) Complex Stabilized with Dianionic Organic Amide Ligand

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For several years, the design of inexpensive non-porphyrin-type inorganic materials for uses in catalytic oxidation reactions has been of interest.[1-4] An approach to this area is to develop the oxidation chemistry of transition-metal–oxo and –nitrido complexes with the oxidation-resistant polyanionic chelating ligands.[2] Following this approach, we have discovered that the manganese(III)[1a] and osmium(III) complexes[1b] of dianionic organic amide ligands such as bpb (H_2bpb = 1,2-bis(2-pyridinecarboxamido)benzene][5] possess rich oxidation chemistry. As part of our work, we set forth to investigate the chemistry of high-valent chromium complexes with the bpb ligand. In this contribution, we describe the synthesis and molecular structure of a nitridochromium(V) complex of bpb, which is a close analogy of a (tetraphenylporphyrinato)nitridochromium(V) complex reported a few years ago.[6]

Experimental Section

Synthesis of Na[Cr^{III}(bpb)(N_3)$_2$] and [Cr^V(bpb)N]. A suspension of [Cr(bpb)Cl]·$x$$H_2O$[7] (0.5 g) and NaN_3 (0.6 g) in acetone (60 mL) was heated under reflux for 3 h. After the reaction, the solution was filtered to remove the insoluble NaCl and NaN_3. The filtrate was rotatory-evaporated to dryness to give a brown Na[Cr(bpb)(N_3)$_2$] solid, which could be recrystallized by slow diffusion of diethyl ether into an acetonitrile solution of the crude sample (yield ~80%). Anal. Calcd for Na[Cr(bpb)(N_3)$_2$]·$^1/_2$$H_2O$: C, 44.6; H, 2.7; N, 28.9. Found: C, 45.1; H, 2.9; N, 28.4. IR (Nujol): $\nu(N_3)$ 2040 cm^{-1}. Λ_M in methanol: 78.4 Ω^{-1} mol^{-1} cm^2.

An acetonitrile solution of Na[Cr(bpb)(N_3)$_2$] (0.2 g in 30 mL) in a quartz tube was degassed with argon for 10 min and then sealed with a rubber septum. The solution was irradiated by using an Annular photoreactor (Applied Photophysics Model APQ 40) equipped with a 400-W medium-pressure short-arc lamp for 36 h. During the photolysis, reddish orange crystals gradually deposited on the wall of the quartz tube. After the reaction was complete, the product was filtered off and washed with water and acetone (yield ~70%). Anal. Calcd for [Cr^V(bpb)N]: C, 56.5; H, 3.2; N, 18.3. Found: C, 56.2; H, 3.4; N, 18.2. IR (Nujol mull): ν(Cr≡N) 1015 cm^{-1}. μ_{eff}: 1.93 μ_B (solid sample, Guoy method).

X-ray Crystal Structure of [Cr^V(bpb)N]. Crystal Data: $C_{18}H_{12}N_5O_2Cr$, reddish orange crystal from dimethylformamide and benzene mixture, M_r = 382.33; monoclinic, space group $P2_1$, a = 6.025 (1) Å, b = 13.321 (1) Å, c = 9.838 (1) Å, β = 90.59 (1)°, V = 786.2 Å^3, D_{measd} = 1.60 g cm^{-3}, Z = 2, D_{calcd} = 1.615 g cm^{-3}, $F(000)$ = 390, μ(Mo Kα) = 7.3 cm^{-1}; crystal dimensions 0.09 × 0.22 × 0.54 mm.

Intensities (h, $\pm k$, $\pm l$; 3766 reflections measured, 1803 unique data, 1628 observed data with $|F_o| > 3\sigma|F_o|$) were measured at 296 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) by using the ω–2θ variable-scan (0.91–5.50° min^{-1}) technique in the bisecting mode up to $2\theta_{max}$ = 54°. Cell parameters were obtained by a least-squares fit of 25 accurately centered reflections with 18.6° < 2θ < 31.8°. Data were corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by Patterson and difference Fourier syntheses and refined by the full-matrix least-squares method.[8] All hydrogen atom positions were calculated geometrically (C–H = 0.95 Å), and the atoms were assigned fixed isotropic temperature factors (B = 5.0 Å^2) and allowed to ride on the parent carbon atoms throughout the refinements. The refinement converged with R = 0.023, R_w = 0.031. The goodness of fit is 1.053, and the shift is less than 0.010σ. The residual extrema in the final difference Fourier map were 0.234 and −0.188 e Å^{-3}, respectively. All programs were taken from the Structure Determination Package (SDP)[9] and run on a MicroVax II computer. Final positional and thermal parameters of non-hydrogen atoms are tabulated in Table I. Selected bond distances and angles are listed in Table II. Tables of hydrogen atomic coordinates, anisotropic thermal parameters, the least-squares plane, and structure factors are available as supplementary material.

Table I. Positional[a] and Thermal Parameters[b] for Non-Hydrogen Atoms in [Cr^V(bpb)N] with Esd's in Parentheses

atom	x	y	z	B_{eq}, Å^2
Cr	11627 (5)	0	17377 (3)	2.169 (5)
O(1)	2256 (4)	−2462 (2)	−601 (2)	4.53 (5)
O(2)	2812 (4)	−503 (3)	5712 (2)	4.93 (5)
N	2468 (4)	921 (2)	1183 (2)	3.04 (4)
N(1)	2792 (3)	−466 (2)	3359 (2)	2.57 (4)
N(2)	2544 (3)	−1218 (2)	1024 (2)	2.54 (4)
N(3)	−991 (3)	−319 (2)	135 (2)	2.58 (4)
N(4)	−751 (3)	629 (2)	3273 (2)	2.53 (4)
C(1)	4505 (4)	−1153 (2)	3089 (3)	2.58 (4)
C(2)	6272 (4)	−1402 (2)	3963 (3)	3.07 (5)
C(3)	7840 (4)	−2091 (3)	3522 (3)	3.77 (6)
C(4)	7663 (5)	−2535 (3)	2266 (3)	3.68 (5)
C(5)	5921 (4)	−2300 (2)	1378 (3)	3.12 (5)
C(6)	4355 (4)	−1590 (2)	1791 (3)	2.55 (4)
C(7)	1636 (4)	−1685 (2)	−48 (2)	2.85 (5)
C(8)	−407 (4)	−1149 (2)	−558 (2)	2.66 (4)
C(9)	−1654 (5)	−1515 (3)	−1640 (3)	3.45 (5)
C(10)	−3569 (5)	−1005 (3)	−2015 (3)	3.74 (6)
C(11)	−4133 (4)	−144 (3)	−1343 (3)	3.60 (6)
C(12)	−2805 (4)	187 (2)	−264 (3)	3.26 (6)
C(13)	−2584 (5)	1195 (2)	3150 (3)	3.31 (5)
C(14)	−3714 (5)	1548 (3)	4284 (3)	3.64 (6)
C(15)	−2936 (5)	1312 (3)	5557 (3)	3.65 (5)
C(16)	−1036 (5)	737 (3)	5691 (3)	3.27 (5)
C(17)	30 (4)	413 (2)	4527 (2)	2.61 (4)
C(18)	2064 (4)	−240 (2)	4605 (2)	2.87 (5)

[a] $\times 10^5$ for Cr; $\times 10^4$ for other non-hydrogen atoms. [b] $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}(a_i^* a_j^*)\mathbf{a}_i\cdot\mathbf{a}_j$.

Table II. Selected Bond Lengths (Å) and Angles (deg) for [Cr^V(bpb)N] with Esd's in Parentheses

Cr–N	1.560 (2)	N(1)–C(18)	1.340 (3)
Cr–N(1)	1.965 (3)	N(2)–C(6)	1.409 (3)
Cr–N(2)	1.957 (2)	N(2)–C(7)	1.338 (3)
Cr–N(3)	2.075 (2)	N(3)–C(8)	1.348 (3)
Cr–N(4)	2.085 (3)	N(3)–C(12)	1.339 (3)
O(1)–C(7)	1.229 (4)	N(4)–C(13)	1.342 (3)
O(2)–C(18)	1.225 (3)	N(4)–C(17)	1.346 (3)
N(1)–C(1)	1.406 (3)		
N(1)–Cr–N	106.5 (2)	Cr–N(1)–C(18)	120.4 (2)
N(2)–Cr–N	108.0 (2)	C(1)–N(1)–C(18)	124.5 (2)
N(3)–Cr–N	102.1 (2)	Cr–N(2)–C(6)	115.4 (2)
N(4)–Cr–N	102.9 (2)	Cr–N(2)–C(7)	119.8 (2)
N(1)–Cr–N(2)	79.54 (9)	C(6)–N(2)–C(7)	124.6 (2)
N(1)–Cr–N(3)	148.74 (9)	Cr–N(3)–C(8)	112.9 (2)
N(1)–Cr–N(4)	79.29 (8)	Cr–N(3)–C(12)	128.4 (2)
N(2)–Cr–N(3)	79.77 (8)	C(8)–N(3)–C(12)	118.7 (2)
N(2)–Cr–N(4)	146.4 (1)	Cr–N(4)–C(13)	128.4 (2)
N(3)–Cr–N(4)	106.64 (8)	Cr–N(4)–C(17)	112.8 (2)
Cr–N(1)–C(1)	114.4 (2)	C(13)–N(4)–C(17)	118.8 (2)

Results and Discussion

The synthesis of [Cr^V(bpb)N] follows similar procedures for [Cr^V(TTP)N] (H_2TTP = 5,10,15,20-tetratolylporphyrin)[6] and

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(1) (a) Che, C. M.; Cheng, W. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1443. (b) Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Ibid.* **1986**, 200. (c) Che, C. M.; Cheng, W. K.; Leung, W. H.; Mak, T. C. W. *Ibid.* **1987**, 418.

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(7) Reaction of anhydrous $CrCl_3$ with H_2bpb in refluxing dimethylformamide for 4 h yielded [Cr(bpb)Cl]·$x$$H_2O$ in high yield.

(8) The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/|\sigma^2(I) + (0.04F_o^2)^2|$.

(9) Frenz, B. A. In *Enraf*-Nonius *Structure Determination Package/SDP Users Guide*: Enraf-Nonius, Delft, The Netherlands, 1985.

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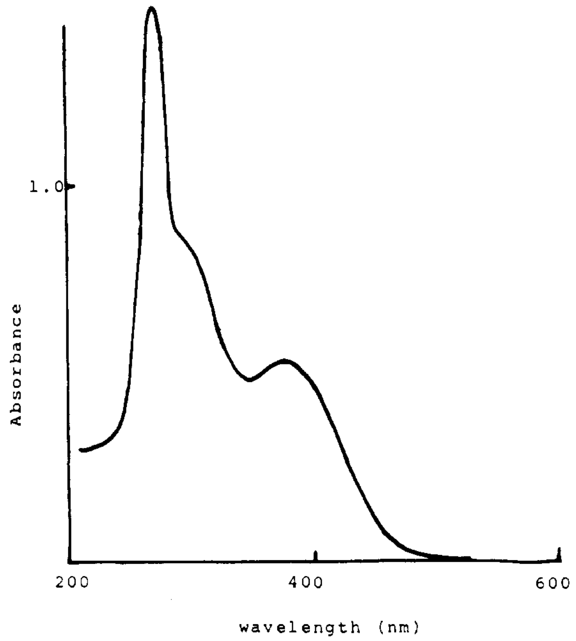

Figure 1. Electronic spectrum of [Cr$^{\mathrm{V}}$(bpb)N] in dimethylformamide.

[Cr$^{\mathrm{V}}$(salen)N] (H_2salen = *N,N'*-bis(salicylidene)ethylenediamine)[10] involving photolysis of chromium(III) azides. The [Cr$^{\mathrm{V}}$(bpb)N] complex is only slightly soluble in most common organic solvents and hence easily separated out from Na[Cr$^{\mathrm{III}}$(bpb)$(N_3)_2$]. It is stable in the solid state and in fluid solution. Its IR spectrum shows the absence of ν(N–H) stretch in the 3000–3500-cm^{-1} region, indicating that the coordinated amide is in the deprotonated form. An extra intense peak at 1015 cm^{-1}, which is absent in the IR spectrum of Na[Cr(bpb)$(N_3)_2$], is attributed to the ν(C$\equiv$N) stretch. For the [Cr$^{\mathrm{V}}$(TPP)N] and [Cr$^{\mathrm{V}}$(salen)N] complexes, the corresponding ν(Cr$\equiv$N) stretches are at 1017 cm^{-1}.[6,10] As expected for the d^1-metal system, it is paramagnetic with a μ_{eff} of 1.93 μ_{B}, which is slightly higher than the spin-only value of one unpaired electron. The optical spectrum (Figure 1) of the Cr(V) complex in dimethylformamide shows intense absorption bands in the 400–250-nm region, possibly arising from the ligand (bpb) to metal (Cr(V)) charge-transfer transitions.

There are relatively few structures of chromium(V) complexes in the literature.[6,11] Figure 2 shows the atomic numbering scheme and the ORTEP drawing of the [Cr$^{\mathrm{V}}$(bpb)N] molecule. The structure features the first example of a chromium(V) complex with organic amide ligands. The complex is five-coordinated, as a consequence of the large σ-trans effect of the N^{3-} group. The salient feature of the structure is that the chromium atom is located 0.508 Å above the mean plane of the four nitrogen atoms. This is likely attributed to the large Coulombic repulsive effect between the Cr$\equiv$N group and bpb ligand. A similar structural feature has also been found with other Cr(V) complexes such as [Cr(TTP)N][6] and K[OCr$(O_2CCOMeEt)_2$]·H_2O.[11] Consistent with that of a formal triple bond, the measured Cr$\equiv$N bond distance of 1.560 (2) Å is very short and virtually identical with that found in [Cr$^{\mathrm{V}}$(TTP)N] (1.565 Å).[6] The average Cr–N(amide) bond distance is 1.961 (2) Å, which is comparable to the Cr–N(peptide) bond distance of 1.956 (7) Å in [Cr(Gly-H$_{-1}$Gly)$_2^-$][12] but slightly shorter than that in [Cr(H(chba-Et))$(py)_2]_2$·2py (2.030 Å).[13] The average Cr–N(pyridine) bond length is ca 0.07 Å longer than the average Cr–N(amide) bond length, in agreement with the fact that the deprotonated amide group is a very strong σ-donor. As with other metal–bpb complexes,[5] the N(amide) atoms, N(1) and N(2), are sp^2 hybridized with the C(18)–N(1)–C(1) and C(6)–N(2)–C(7) bond angles being 124.5 (2) and 124.6 (2)°, respectively. The bond angles and bond distances of the bpb ligand are normal.

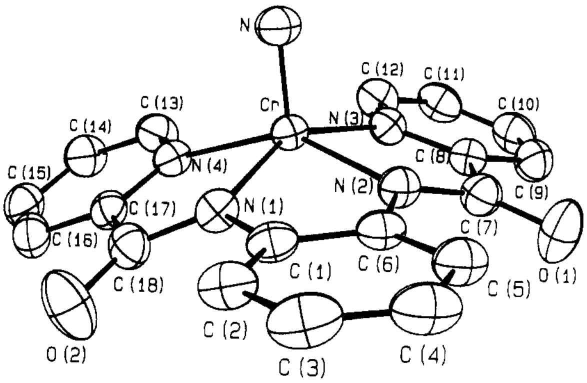

Figure 2. ORTEP drawing of the [Cr$^{\mathrm{V}}$(bpb)N] molecule showing the atomic numbering scheme.

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Registry No. Na[Cr(bpb)$(N_3)_2$], 114720-38-6; Cr$^{\mathrm{V}}$(bpb)N, 114720-39-7; Cr(bpb)Cl, 114720-40-0; N_3^-, 14343-69-2.

Supplementary Material Available: Tables of hydrogen atomic coordinates, anisotropic thermal parameters, bond lengths and angles for non-hydrogen atoms, and the least-squares plane (4 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Reactivity Trends and Volumes of Activation for Dissociation of [1,8-Bis((2-pyridylmethylene)amino)-3,6-diazaoctane]iron(II) by Hydroxide Ion in Aqueous Alcohols and Aqueous Acetone

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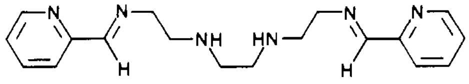
There are many examples of Schiff-base, low-spin complexes of iron(II).[2,3] The hexadentate ligand 1,8-bis((2-pyridylmethylene)amino)-3,6-diazaoctane (hxsb, **1**) forms with iron(II)



hxsb, **1**

a complex[3] that is particularly inert to dissociation by nucleophiles.[4] Kinetic studies of the dissociation of Fe(hxsb)$^{2+}$ by hydroxide ion in aqueous solution over a range of pressure yielded a volume of activation, ΔV^*, of +13 cm^3 mol^{-1} at 298.2 K.[4b,5] The expected value of ΔV^* for the bimolecular reaction in the absence of a solvent, i.e. intrinsic, is −10 cm^3 mol^{-1}.[6] Desolvation of electrostricted water from the hydroxide ion as it attacks the iron

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