Tris{bis[imino(methoxy)methyl]aminato}cobalt(III): An Electronic Analogue of Tris(β-diketonates)†

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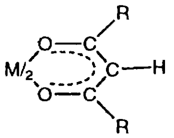
The cobalt(III) complex [Co(HNCOMeNCOMeNH)$_3$], *i.e.* [CoL$_3$], has been prepared from the copper precursor, [CuL$_2$] in a Me$_2$SO–CoS suspension. Its crystal and molecular structure has been determined by X-ray diffraction (R = 0.0577). The crystal consists of isolated molecules exhibiting a {CoN$_6$} chromophore. In solution the complex is ESR silent, evidencing the absence of Co^{II} or Cu^{II}. The ligand L generates a rather strong ligand field (Δ/hc = 21 200 cm^{-1}) as follows from an analysis of the electronic spectra.

Recently it was found that the β-diketonates **1** have their isoelectronic analogues **2** exemplified by the complex [Cu(HNCOMeNCOMeNH)$_2$].[1,2] This complex is formed from the system Cu^{II}–dicyanamide–pyridine(py)–methanol–water (molar ratio 1 : 2 : 25 : 30 : 60) by a nucleophilic addition of a methanol molecule to co-ordinated dicyanamide NH(CN)$_2$, *i.e.* to the β-C site of dicyanamide activated by co-ordination. The reaction is catalysed in good yields only by copper(II) salts, represented by pyridine complexes, under moderate conditions. A similar reaction involving zinc(II) salts, but proceeding under more drastic conditions, has also been reported.[3] No reaction is observed with salts of Co^{II}, Ni^{II}, Pd^{II} and Pt^{II}. Thus we focused on an indirect preparation of analogous metal complexes using the copper(II) complex as a precursor. There is no evidence for nucleophilic addition in the system Co^{II}–KN(CN)$_2$–py–MeOH–water–H$_2$O$_2$. However, using a suspension of CoS in dimethyl sulfoxide (dmso) we were able, to prepare a cobalt(III) analogue, [Co(HNCOMeNCOMeNH)$_3$], **3**. This complex has been studied spectroscopically and its crystal and molecular structure determined.



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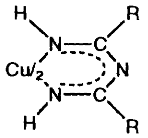

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Experimental

Synthesis.—The chemicals used were of analytical grade. A dimethyl sulfoxide solution (40 cm^3) of [Cu(HNCOMeNCOMeNH)$_2$] (1.0 g, violet-red crystals) was treated under reflux for 5 d at 50 °C with a suspension of CoS (1.0 g) under aerobic conditions. After filtration the solution was allowed to stand for 6 months to give a mixture of crystals of the original complex and red-brown crystals of **3** of different habit (Found: C, 32.05; H, 5.40; N, 28.05. Calc. for $C_{12}H_{24}CoN_9O_6$: C, 30.70; H, 5.10; N, 26.85%). The discrepancies can be explained by presence of some of the copper precursor. The ESR spectrum was recorded using an X-band spectrometer (Bruker, model ER 200 D SRC). A dmso solution of the crystalline material produces an ESR signal almost identical with that of the copper precursor.[2] A carefully separated single crystal of **3** dissolved in dmso was ESR silent showing neither traces of copper(II) nor cobalt(II) centres. The electronic spectra were recorded at room temperature in a MgO tablet (reflectance spectrum, Beckman 5240) and dmso solution (absorption spectrum, Carl-Zeiss, M800 spectrometer).

Crystallography.—*Crystal data.* $C_{12}H_{24}CoN_9O_6$, M = 3598.66, monoclinic, space group $C2/c$ (no. 15), a = 18.852(4), b = 17.241(3), c = 14.752(3) Å, β = 126.77(3)°, U = 3840.9 Å^3, Z = 8, D_c = 1.554 g cm^{-3}. Red-brown crystals of dimensions 0.15 × 0.19 × 0.40 mm, μ(Mo-Kα) = 0.94 mm^{-1}, $F(000)$ = 1872.

Data collection and processing. SYNTEX P2$_1$ diffractometer, θ–2θ scan mode, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); 4694 reflections measured ($1 < \theta < 27.5°$, $20 < h < 19$, $-22 < k < 22$, $0 < l < 16$), 4161 unique [merging R = 0.0431 after absorption correction (maximum, minimum transmission factors = 1.00, 0.75)], giving 2172 with $F > 4\sigma(F)$.

Structure analysis and refinement. All non-hydrogen atoms were localized by the Patterson method and a subsequent Fourier synthesis. Full-matrix least-squares refinement on F^2 with all non-hydrogen atoms anisotropic and hydrogens constrained [CH$_3$, C–H 0.96 Å; NH; hydrogen on the external bisector Co–N–C angle] with U(H) = 1.2 U_{eq} (C or N). The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 4.57P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final R_1 and wR_2 values were 0.0577 and 0.1305. Programs and scattering factor data according to refs. 4–9. Final fractional atomic coordinates are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal and Molecular Structure.—The crystal structure of complex **3** consists of discrete molecules (Fig. 1). Owing to the absence of symmetry operations, the molecular symmetry is C_1. The cobalt cation is octahedrally co-ordinated by six nitrogen atoms of three HNCOMeNCOMeNH anions, Co–N 1.883–1.899 Å. The metal–ligand moiety forms a six-membered metallocycle as in the analogous copper(II) complex. The NH–C distances of 1.262(5)–1.287(6) Å and N–C 1.302(6)–1.326(5) Å

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

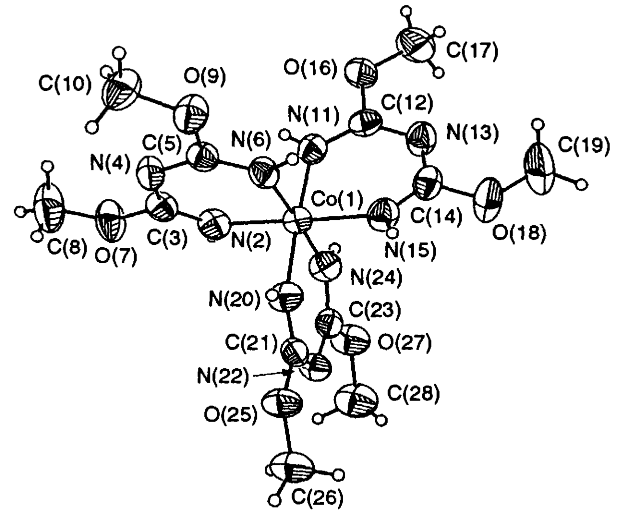

Fig. 1 Molecular structure of [Co(HNCOMeNCOMeNH)$_3$] with atom numbering. The thermal ellipsoids are drawn at the 50% probability level

Table 1 Final atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for complex **3**

Atom	*x*	*y*	*z*
Co(1)	3530(1)	2965(1)	2871(1)
N(2)	3712(2)	1941(2)	3417(3)
C(3)	3739(3)	1326(3)	2975(4)
N(4)	3754(3)	1248(2)	2093(3)
C(5)	3721(3)	1880(3)	1574(4)
N(6)	3603(2)	2584(2)	1727(3)
O(7)	3780(3)	664(2)	3491(3)
C(8)	3749(5)	−50(3)	3004(5)
O(9)	3809(2)	1782(2)	739(3)
C(10)	3976(4)	1025(3)	544(4)
N(11)	4762(2)	3161(2)	3828(3)
C(12)	5146(3)	3820(3)	4018(4)
N(13)	4786(3)	4504(2)	3623(3)
C(14)	3937(3)	4547(3)	2826(4)
N(15)	3374(3)	3989(2)	2336(3)
O(16)	6038(2)	3789(2)	4722(3)
C(17)	6509(4)	4504(3)	5029(5)
O(18)	3582(2)	5251(2)	2437(3)
C(19)	4147(4)	5903(3)	2934(5)
N(20)	2287(2)	2819(2)	1929(3)
C(21)	1750(3)	2924(3)	2169(3)
N(22)	1917(2)	3174(2)	3122(3)
C(23)	2730(3)	3360(2)	3959(4)
N(24)	3433(3)	3312(2)	4014(3)
O(25)	895(2)	2770(2)	1325(3)
C(26)	257(3)	2878(3)	1522(4)
O(27)	2864(2)	3645(2)	4897(3)
C(28)	2128(4)	3712(4)	4926(5)

respectively indicate a strongly delocalized π-bonding system (Table 2).

The donor nitrogen atom–hydrogen contacts are quite short, N–H 0.68–0.85 Å. As these hydrogen atoms are expected to be acidic, the short contacts indicate the separation of electron-density maxima rather than the nuclear positions. They are slightly longer than the corresponding counterparts found in the copper(II) analogue, where N–H 0.69 Å.

On the ordinate N(20)–H(20) ··· O(9$^{\text{I}}$) (equivalent position I: $(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z)$, the individual contacts are N(20)–H(20) 0.80(5), H(20) ··· O(9$^{\text{I}}$) 2.59(4), N(20) ··· O(9$^{\text{I}}$) 3.240(5) Å and the angle N(20)–H(20)–O(9$^{\text{I}}$) 140(1)°. This is evidence for hydrogen bonding in the crystal structure.

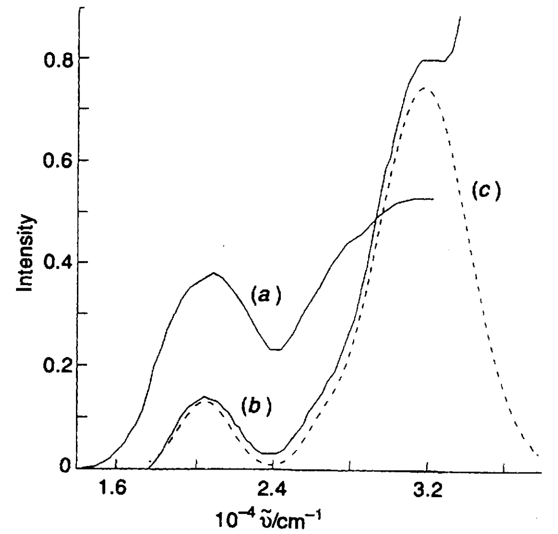

Fig. 2 Electronic spectrum of complex **3**: (*a*) reflectance spectrum in MgO tablet; (*b*) absorption spectrum in dmso solution; (*c*) deconvolution (dashed)

Table 2 Selected bond lengths (Å) and valence angles (°)

Co(1)–N(2)	1.884(4)	C(12)–N(13)	1.310(6)
Co(1)–N(6)	1.891(4)	C(12)–O(16)	1.349(5)
Co(1)–N(11)	1.890(4)	N(13)–C(14)	1.302(6)
Co(1)–N(15)	1.883(4)	C(14)–N(15)	1.287(6)
Co(1)–N(20)	1.895(4)	C(14)–O(18)	1.338(5)
Co(1)–N(24)	1.899(4)	O(16)–C(17)	1.426(6)
N(2)–C(3)	1.262(5)	O(18)–C(19)	1.414(6)
C(3)–N(4)	1.326(5)	N(20)–C(21)	1.268(5)
C(3)–O(7)	1.347(5)	C(21)–N(22)	1.316(5)
N(4)–C(5)	1.311(5)	C(21)–O(25)	1.347(5)
C(5)–N(6)	1.279(5)	N(22)–C(23)	1.308(5)
C(5)–O(9)	1.348(5)	C(23)–N(24)	1.280(5)
O(7)–C(8)	1.409(6)	C(23)–O(27)	1.343(5)
O(9)–C(10)	1.410(5)	O(25)–C(26)	1.409(5)
N(11)–C(12)	1.284(5)	O(27)–C(28)	1.416(6)
N(20)–Co(1)–N(24)	87.6(2)	N(6)–Co(1)–N(15)	91.6(2)
N(15)–Co(1)–N(24)	90.1(2)	N(6)–Co(1)–N(11)	90.9(2)
N(15)–Co(1)–N(20)	90.2(2)	N(2)–Co(1)–N(24)	90.3(2)
N(11)–Co(1)–N(24)	90.5(2)	N(2)–Co(1)–N(20)	91.0(2)
N(11)–Co(1)–N(20)	177.1(2)	N(2)–Co(1)–N(15)	178.7(2)
N(11)–Co(1)–N(15)	87.7(2)	N(2)–Co(1)–N(11)	91.2(2)
N(6)–Co(1)–N(24)	177.8(2)	N(2)–Co(1)–N(6)	87.9(2)
N(6)–Co(1)–N(20)	91.0(2)		

Electronic Spectra.—According to Fig. 2, within the range of 11 000–33 300 cm^{-1} the spectrum exhibits two broad overlapping bands centred at 31 700 (315) and 20 400 cm^{-1} (490 nm) with a shoulder at 26 400 cm^{-1} (379 nm). Deconvolution of the experimental spectrum to gaussian curves was possible when the higher-energy part was completed by a symmetric estimate (Fig. 2). The gaussian curves were characterized by the following parameters: position of the maximum, $\nu_{\max}$, height, $I_{\max}$, and half-width σ. The deconvolution results are presented in Table 3.

For the interpretation of the electronic spectra we used the standard coordinate system for an octahedral chromophore where the individual central atom d orbitals span the irreducible representations $e_g(d_{x^2-y^2}, d_{z^2})$ and $t_{2g}(d_{xz}, d_{yz}, d_{xy})$. The possible electronic transitions are to $^1T_{1g}$ and $^1T_{2g}$ (low-spin) and $^3T_{1g}$ and $^3T_{2g}$ (high-spin, spin-forbidden) excited states, respectively. If a lower symmetry D_3 is relevant the energy states are further split (see Fig. 3) but their separation is not seen in the absorption spectra. They may be differentiated in circular dichroism spectra.[10]

The spectrum of complex **3** can be compared with those published for $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine) and $[Co(ox)_3]^{3-}$ (ox = oxalate). The transition energies $\Delta E(^1A$

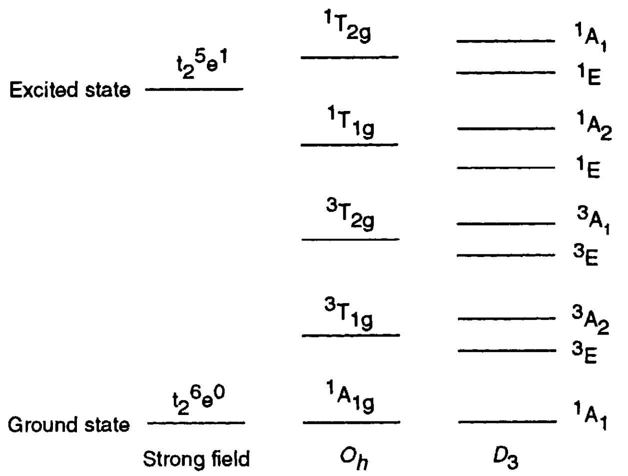

Fig. 3 Energy terms in O_h and D_3 environments for a 3d^6 configuration

Table 3 Deconvolution of electronic spectra

Number of gaussians	Intensity, I	Half-width σ/cm^{-1}	Maximum $\tilde{\nu}_{max}$/cm^{-1}
2	0.130	1 890	20 400
	0.738	3 460	31 700
3	0.130	1 880	20 430
	0.049	1 350	26 460
	0.746	3 360	31 750

Table 4 Crystal field parameters (cm^{-1})

	Transitions[a]		Parameters[b]	
Complex	E_1	E_2	Δ	B
$[Co(ox)_3]^{3-}$	16 500	23 800	17 190 (18 000)	548 (540)
$[Co(en)_3]^{3+}$	21 400	29 500	22 430 (23 200)	587 (590)
$[Co(acac)_3]$[c]	16 800	25 000	17 360 (20 700)	634 (440)
$[CoL_3]$[d]	20 400	31 700	21 160	815

[a] $E_1 = \Delta E(^1A_{1g} \longrightarrow {}^1T_{1g})$, $E_2 = \Delta E(^1A_{1g} \longrightarrow {}^1T_{2g})$. [b] $\Delta = 84B^2/(16B + E_1 - E_2)$, $B = [-b - (b^2 - 4ac)^{\frac{1}{2}}]/2a$ with $a = 11\,848$, $b = 536E_1 - 1208E_2$, $c = (E_1 - E_2)(E_1 - 43E_2)$. Values in parentheses according to refs. 13–15. [c] acac = Acetylacetonate. [d] $L^- = HNCOMeNCOMeNH^-$.

$\longrightarrow {}^1T_2)/hc = 29\,500$, $\Delta E(^1A \longrightarrow {}^1T_1)/hc = 21\,400$, and $\Delta E(^1A \longrightarrow {}^3T_1)/hc = 13\,700$ cm^{-1} were found for the former and $\Delta E(^1A \longrightarrow {}^1T_2)/hc = 23\,800$ and $\Delta E(^1A \longrightarrow {}^1T_1)/hc = 16\,500$ cm^{-1} for the latter.[11,12] Using the well known crystal-field formulae (1) and (2) (Δ being the crystal-field-splitting parameter)

$$\Delta E(^1A \longrightarrow {}^1T_1) = \Delta - C + (86B^2/\Delta) \quad (1)$$

$$\Delta E(^1A \longrightarrow {}^1T_2) = \Delta + 16B - C + (2B^2/\Delta) \quad (2)$$

and assuming that the Racah parameters obey the relation $C = 4B$, we can utilize the electronic transitions to calculate Δ and B (Table 4). The spin-forbidden transitions can be represented by equations (3) and (4).[13] Therefore the evaluation of parameters Δ, B and

$$\Delta E(^1A \longrightarrow {}^3T_1) = \Delta - 3C + (50B^2/\Delta) \quad (3)$$

$$\Delta E(^1A \longrightarrow {}^3T_2) = \Delta + 8B - 3C + (14B^2/\Delta) \quad (4)$$

eventually C slightly depends on which transitions and which equations are used.

Based on the calculated value $\Delta/hc = 21\,200$ cm^{-1} it may be concluded that the present ligand generates a rather strong crystal field. Reduction of the B value relative to the free-ion value ($B/hc = 1400$ cm^{-1}) indicates, in general, a decreased interelectron repulsion due to the covalency. The calculated value of $B/hc = 815$ cm^{-1} for **3**, however, is higher than that for other complexes of the $[CoL_3]$ type where 600 cm^{-1} is typical. This shows an increased d-electron repulsion probably due to the stronger donation effect of the ligand in **3**.

Theoretical

Molecular Orbital Calculations.—The complete structure of complex **3** has been investigated by the *ab initio* linear combination of atomic orbitals self-consistent-field molecular-orbital approach (MO-LCAO-SCF) with the double-zeta basis set (Wachters basis set[16] for Co and Huzinaga sets for main-row elements).

Charge distribution. The cobalt central atom has a d-orbital population of d$^{6.79}$ (compared with d$^{6.0}$ for Co^{III}) which indicates an increased donation ability of the ligands and may explain the larger B value for **3** relative to other $[CoL_3]$ type complexes. The charge distribution shows that the N–H bonds are polar as $Q(H) = +0.07$ to $+0.19$ e (Mulliken population analysis); thus the hydrogen atoms bonded to donor nitrogens can be considered as acidic. A similar situation has been found in the copper analogue and is consistent with the very short N–H contacts observed in the crystal structure.

Complex stability. Based on the *ab initio* values of the total molecular energy for the free aminate L$^-$, Co^{3+} ion and the complex $[CoL_3]$ **3**, the stabilization energy has been calculated as $\Delta E(3) = E(3) - E(Co^{3+}) - 3E(L^-) = -23.16$ eV. The ligand L$^-$ was subject to a geometry optimization in the double-zeta (+ polarization functions) basis set. A similar calculation has been done for the $[CuL_2]$ complex, hence $\Delta E(CuL_2) = E(CuL_2) - E(Cu^{2+}) - 2E(L^-) = -15.69$ eV. These values indicate the high stability of the respective complexes, $[CoL_3]$ being more stable than $[CuL_2]$. On the basis of these data one can rationalize why the $[CoL_3]$ complex can be prepared from the $[CuL_2]$ precursor.

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