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Synthesis, Structure, and Properties of an Imidazolate-Bridged Copper(II)–Cobalt(III) Complex

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The synthesis of $[(\mathrm{PMDT})\mathrm{Cu(im)Co(NH_3)_5}](\mathrm{ClO_4})_4$, where PMDT = 1,1,4,7,7-pentamethyldiethylenetriamine and im = imidazolate anion, is reported. Single-crystal X-ray diffraction studies show this new, heterobimetallic complex to crystallize in the monoclinic space group $P2_1/c$ with a = 15.694 (4) Å, b = 15.771 (4) Å, c = 14.112 (3) Å, β = 112.11 (2)°, and Z = 4. The cobalt(III) center has five equivalent $\mathrm{Co{-}NH_3}$ bonds ranging from 1.957 (7) to 1.983 (5) Å in length and a Co–N(imidazolate) bond distance of 1.933 (5) Å. The copper(II) geometry is D_{2d} distorted square planar with a Cu–N(imidazolate) bond of 1.954 (6) Å and a long axial Cu···O(perchlorate) contact of 2.886 (7) Å. Variable-temperature magnetic susceptibility studies of the solid complex reveal Curie-type behavior with an effective moment of 1.72 μ_B and g_{av} = 2.07. The latter agrees with the value determined by solid-state electron spin resonance measurements. Through a combination of pH-dependent frozen-solution electron spin resonance, electronic spectral, and potentiometric titration studies, the imidazolate bridge was shown to split at the copper(II) site in protic media. The pK_a values for the mononuclear components $[(\mathrm{NH_3})_5\mathrm{Co(imH)}]^{3+}$ and $[(\mathrm{PMDT})\mathrm{Cu(OH_2)}]^{2+}$, generated from the bridged complex in solution, are in good agreement with those reported previously.

The coordination chemistry of bridged, binuclear transition-metal complexes has been the subject of extensive study.[1,2] Recent interest in this topic has been stimulated by the efforts of bioinorganic chemists to synthesize model compounds for the coordination sites of metallobiomolecules.[3] Particularly intriguing are heterobinuclear complexes[4] where the influence of one transition metal on the physical and chemical properties of its neighbor can be assessed. Heterobimetallic centers are known to occur in bovine erythrocyte superoxide dismutase (Cu, Zn)[5] and cytochrome *c* oxidase (Cu, Fe).[6] Their role in these redox enzymes is not fully understood at present.

The imidazole (imH) ring of the amino acid histidine is a ubiquitous ligand in chemical and biological systems.[7] Its conjugate base, the imidazolate (im) ion, bridges copper(II) and zinc(II) in bovine erythrocyte superoxide dismutase (BESOD).[5] An imidazolate-bridge splitting and reformation cycle has been postulated[8] to occur during enzyme turnover in an effort to rationalize the role of the zinc. This proposal is difficult to test through direct studies of the enzyme, however, because of the very rapid rate of the superoxide dismutase reaction.[9] Moreover, the metal binding properties of copper–zinc superoxide dismutase are quite dependent on pH[10,11] and most likely involve the bridging imidazolate ion.

In order to elucidate the properties of imidazolate-bridged bimetallic centers in simpler systems, several model compounds have been synthesized and characterized. At present $[\mathrm{MM'(im)}]^{n+}$ complexes have been isolated for M = M′ = Cu(II),[12-17] $\mathrm{CH_3Hg^{II}}$,[18] Ru(III),[19] Co(III),[19] Mn(porphyrin),[20] and Fe(porphyrin),[20] for M = Ru(III) and M′ = Co(III), and for M = Ru(II) and M′ = Ru(III).[19] Solution studies of the dicopper(II) complexes have shown that, unless the $[\mathrm{Cu_2(im)}]^{3+}$ moiety is encapsulated in a binucleating macrocycle, the bridge is quite fragile and only exists over a narrow pH range.[12,13,17,21] This work has now been extended to the heterobimetallic center $[\mathrm{Cu^{II}Co^{III}(im)}]^{4+}$ in which, like the copper–zinc SOD's, the copper(II) ion is adjacent to a diamagnetic metal ion that is relatively inaccessible to reactions with anion or solvent. Because of the kinetic inertness of the cobalt(III) center, the imidazolate bridge splitting reaction can only occur at the copper(II) site.

Here we report the synthesis, magnetic properties, molecular structure, and selected solution properties of $[(\mathrm{PMDT})\mathrm{Cu(im)Co(NH_3)_5}](\mathrm{ClO_4})_4$, where PMDT = 1,1,4,7,7-pentamethyldiethylenetriamine. This system was chosen because of the ready availability of the $[\mathrm{Co(NH_3)_5(imH)}]^{3+}$ ion[22] and our previous experience with imidazolate-bridged (diethylenetriamine)copper(II) complexes.[13,17]

Experimental Section and Results

Synthetic Work. The compounds $(\mathrm{PMDT})\mathrm{Cu(ClO_4)_2}\cdot 2\mathrm{CH_3CN}$[23] and $[\mathrm{Co(NH_3)_5(imH)}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$[22] were prepared by literature procedures. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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(1) Groh, S. E. *Isr. J. Chem.* **1976–1977**, *15*, 277–307.

(2) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, 199–220.

(3) Ibers, J. A.; Holm, R. H. *Science* (*Washington, D.C.*) **1980**, *209*, 223–235.

(4) Kahn, O.; Claude, R.; Coudanne, H. *Nouv. J. Chim.* **1980**, 167–172 and references cited therein.

(5) Richardson, J. S.; Thomas, K. A.; Rubin, B. H.; Richardson, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1349–1353.

(6) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206–2210.

(7) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471–517.

(8) (a) Hodgson, E. K.; Fridovich, I. *Biochemistry* **1975**, *14*, 5294–5299. (b) Lippard, S. J.; Burger, A. R.; Ugurbil, K.; Valentine, J. S.; Pantoliano, M. W. *Adv. Chem. Ser.* **1977**, *No. 162*, 251–262. (c) McAdam, M. E.; Fielden, E. M.; Lavelle, F.; Calabrese, L.; Cocco, D.; Rotilio, G. *Biochem. J.* **1977**, *167*, 271–274.

(9) (a) Klug-Roth, D.; Fridovich, I.; Rabani, J. *J. Am. Chem. Soc.* **1973**, *95*, 2786–2790. (b) Fielden, E. M.; Roberts, P. R.; Bray, R. C.; Low, D. J.; Mautner, G. N.; Rotilio, G.; Calabrese, L. *Biochem. J.* **1974**, *139*, 49–60.

(10) Valentine, J. S.; Pantoliano, M. W.; McDonnell, P. J.; Burger, A. R.; Lippard, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4245–4249.

(11) Pantoliano, M. W.; McDonnell, P. J.; Valentine, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 6454–6456.

(12) (a) Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720–5721. (b) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079–2082.

(13) (a) O'Young, C.-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291–7300. (b) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E-i.; Lehn, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 265–266.

(14) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622–2630. (b) Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Ibid.* **1979**, *18*, 141–148.

(15) Mori, W.; Nakahara, A.; Nakao, Y. *Inorg. Chim. Acta* **1979**, *37*, L507–L508.

(16) Hendricks, H. M. J.; Reedjik, J. *Inorg. Chim. Acta* **1979**, *37*, L509–L510.

(17) Katz, R. N.; Kolks, G.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3845–3847.

(18) Evans, C. A.; Rabenstein, D. L.; Geier, G.; Erni, I. W. *J. Am. Chem. Soc.* **1977**, *99*, 8106–8108.

(19) Isied, S. S.; Kuehn, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6754–6756.

(20) (a) Landrum, J. T.; Reed, C. A.; Hatano, K.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3232–3234. (b) Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *Ibid.* **1980**, *102*, 6729–6735.

(21) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7616–7617.

(22) Harrowfield, J. M.; Norris, V.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7282–7289.

0020-1669/81/1320-2928$01.25/0

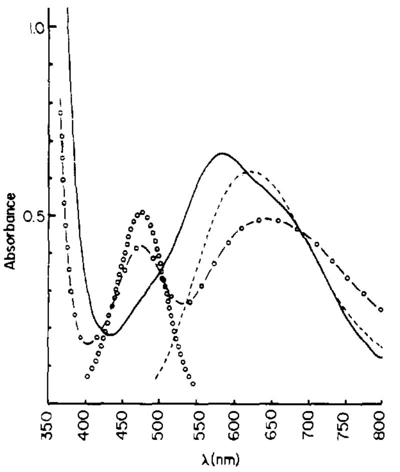

Figure 1. Visible spectra of $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$ in acetonitrile (—) and in acetonitrile containing excess perchloric acid (-o-), of $[(PMDT)Cu(NCCH_3)_2](ClO_4)_2$ (---) in acetonitrile, and of $[Co(NH_3)_5(imH)](ClO_4)_3$ (ooo) in acetonitrile solution.

Preparation of (μ-Imidazolato)-(pentaamminecobalt(III))(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II) Perchlorate. To a solution containing 125 mg (0.24 mmol) each of $[Co(NH_3)_5(imH)](ClO_4)_3 \cdot H_2O$ and Cu(PMDT)-$(ClO_4)_2 \cdot 2CH_3CN$ in 25 mL of refluxing methanol was added 2.6 mL of 0.09 M sodium methoxide in 200 μL aliquots over a period of 1 h. A violet solid precipitated immediately. The solid was isolated by filtration, washed with cold methanol, and dried at room temperature in vacuo. The yield was 67 mg (33%). X-ray diffraction quality crystals were obtained by allowing methylene chloride vapor to diffuse into an acetonitrile solution of the product. Anal. Calcd for $C_{12}H_{41}N_{10}O_{16}Cl_4CoCu$: C, 17.04; H, 4.89; N, 16.56. Found: C, 17.42; H, 4.89; N, 16.36.

Magnetic and Spectroscopic Measurements. Magnetic susceptibility measurements were made in the range 4.2 K $\leq T \leq$ 298 K at 10.6 kOe by the Faraday method with use of a locally constructed balance.[23] The measurement made at 4.2 K was repeated at six different field strengths in the range 3.7–10.6 kOe, showing the absence of ferromagnetic impurities. Diamagnetic corrections were made with use of a tabulation of Pascal's constants.[24] A plot of χ_M^{cor} vs. T^{-1} for solid $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$ was linear with a slope of 0.371 deg cm^3 mol^{-1} and a measured temperature-independent paramagnetism (TIP) of 386 × 10^{-6} cm^3 mol^{-1}. The effective magnetic moment and g values were 1.72 μ_B and 2.07, respectively. A table of observed and calculated temperature-dependent molar susceptibilities is available.[25]

Electron spin resonance spectra were recorded with use of a Varian E-line X-band spectrometer operating between 9.101 and 9.151 GHz. The g values were calibrated with the manganese(II) impurity in strontium oxide (g = 2.0012). The solution spectrum was taken on a sample dissolved in 1:1 (v:v) N,N-dimethylacetamide/methanol to an approximate concentration of 10 mM. The ESR spectrum of solid $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$ at 93 K displayed a single signal at g 2.06, in good agreement with the value from the χ_M^{cor} vs. T^{-1} plot. The frozen-solution (93 K) spectrum of the complex was axially symmetric with $g_\parallel = 2.225$, $g_\perp = 2.024$, and $A_\parallel$ = 168 G. Addition of up to 1 equiv of protons produced small monotonic changes in the spectrum resulting, finally, in values for $g_\parallel$ and $g_\perp$ of 2.243 and 2.030, respectively.

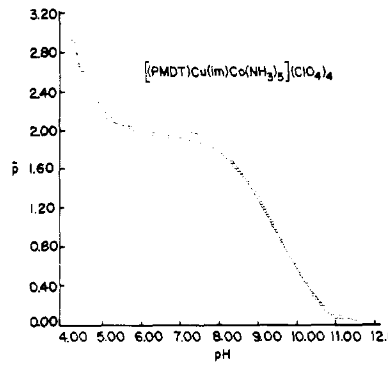

Figure 2. Potentiometric titration for $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$. Open circles represent the experimental points, and the solid line is the fit to the expressions described in the text.

This spectrum is identical with that of the $[(PMDT)Cu(NCCH_3)_2]^{2+}$ ion in the same solvent system which is consistent with cleavage of the imidazolate bridge at the copper(II) binding site.

Electronic spectra were recorded in acetonitrile solutions contained in 1-cm matched quartz cells with use of a Cary-118C spectrophotometer. A series of visible spectra is displayed in Figure 1. The imidazolate-bridged complex exhibits a broad maximum at 585 nm (ϵ = 285 M^{-1} cm^{-1}) in acetonitrile and obeys Beer's law in the 0.25–5.0-mM concentration range. It is also stable in dimethyl sulfoxide solution. Upon addition of excess perchloric acid, however, the 585-nm band disappears and two new peaks occur at 625 and 485 nm. These values correspond approximately to the spectral maxima observed for $[(PMDT)Cu(NCCH_3)_2](ClO_4)_2$ and $[Co(NH_3)_5(imH)](ClO_4)_3$ (Figure 1). The perchloric acid solution was prepared by diluting stock 70% aqueous $HClO_4$ with acetonitrile to 0.10 M concentration.

Potentiometric Titrations. A Radiometer TTT-1C pH meter was used to monitor the pH of aqueous solutions during the potentiometric titrations. Acid (HNO_3, approximately 0.1 N) and base (NaOH, approximately 0.1 N) solutions were prepared with carbon dioxide free, distilled, and deionized water containing enough potassium nitrate to bring the ionic strength to 0.16. The sodium hydroxide solution was standardized with potassium hydrogen phthalate. Sample solutions (approximately 2.5 mM) were prepared in the same manner.

The titration curve of an aqueous solution of the bridged complex from pH 11.2 to 4.5 is shown in Figure 2. Two protons are taken up between pH 11.2 and 6.4. Least-squares fitting of the data to a simple expression derived from the equilibria shown in eq 1 and 2 gave pK_1 = 10.0 and pK_2 = 8.75.

$$K_1 = \frac{[(NH_3)_5Co(im)^{2+}][H^+]}{[(NH_3)_5Co(imH)^{3+}]} \tag{1}$$

$$K_2 = \frac{[(PMDT)Cu(OH)^+][H^+]}{[(PMDT)Cu(OH_2)^{2+}]} \tag{2}$$

The equilibria correspond to the release of protons from $[(NH_3)_5Co(imH)]^{3+}$ and $[(PMDT)Cu(OH_2)]^{2+}$, respectively. Attempts to account for the formation of the imidazolate-bridged complex in these aqueous solution potentiometric titrations (cf. ref 23) were unsuccessful for reasons mentioned below in the Discussion.

Collection and Reduction of X-ray Data. The mauve crystal used for the diffraction study was a multifaceted parallelepiped bounded by (010) and $(0\bar{1}0)$ (0.134 mm apart), (011) and $(0\bar{1}\bar{1})$ (0.234 mm apart), $(0\bar{1}1)$ and $(01\bar{1})$ (0.250 mm apart), and the two pairs $(\bar{1}\bar{1}1)$, $(11\bar{1})$ and $(\bar{1}11)$, $(1\bar{1}\bar{1})$ (each 0.266 mm apart). Open counter ω scans of several strong, low-angle reflections were used to inspect the quality of the data crystal.

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(23) Kolks, G.; Frihart, C. R.; Coughlin, P. K.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 2933.

(24) Drago, R. S. "Physical Methods in Chemistry"; Saunders: Philadelphia, 1977; p 413.

(25) Supplementary material.

Table I. Experimental Details of the X-ray Diffraction Study of $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$

(A) Crystal Parameters[a] at 23 °C

$a = 15.694\ (4)$ Å	mol wt 845.8
$b = 15.771\ (4)$ Å	space group $P2_1/c$
$c = 14.112\ (3)$ Å	$Z = 4$
$\beta = 112.11\ (2)^\circ$	ρ(calcd) = 1.736 g cm^{-3}
$V = 3236.0$ Å^3	ρ(obsd)[b] = 1.736 (4) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_{α_1} = 0.709 30 Å, $\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized
takeoff angle: 2.0°
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
cryst–detector distance: 173 mm
scan technique: coupled ω(cryst)–2θ(counter)
scan width: variable, $\Delta\omega = (0.8 + 0.35 \tan\theta)^\circ$
scan rate: variable from 1.62–20.12° min^{-1} in ω
scan range: $3^\circ \leqslant 2\theta \leqslant 50^\circ$
prescan rejection limit: 1σ
prescan acceptance limit: 100σ
max counting time: 60 s
bkgd measurements: moving cryst–moving detector, 25% added to scan width at both ends of each scan
stds: three reflections $(\bar{2}\bar{3}\bar{6})$, $(\bar{7}25)$, and $(2\bar{2}4)$, measured every 3600 s of X-ray exposure time, showed no decay
no. of reflctns collected: $[3^\circ \leqslant 2\theta \leqslant 30^\circ\ (\pm h,-k,-l),\ 3^\circ \leqslant 2\theta \leqslant 50^\circ\ (\pm h,+k,+l)]$; 7372 reflections, nonspace group extinguished

(C) Treatment of Intensity Data

reduction to F_o and $\sigma(F_o)$: correction for bkgd, attenuator, and Lorentz–polarization of monochromatized X-radiation as described previously[c]
averaging: 842 equivalent pairs in the inner sphere ($2\theta < 30^\circ$); agreement factor $R_{av} = 0.022$
obsd data: 5688 unique reflections of which the 3016 with $F_o > 6\sigma(F_o)$ were used in the structure refinement

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30^\circ$. [b] By suspension in a mixture of bromoform and chloroform. [c] Reference 26.

These peaks showed no structure but were somewhat broad ($\Delta\bar{\omega}_{1/2} = 0.22^\circ$). No better crystals were found, however.

Pertinent information concerning the acquisition of the diffraction data is given in Table I and ref 26. Inspection of the systematic absences in the data list showed the space group to be $P2_1/c$ (C_{2h}^5, No. 14).[27] An absorption correction was not applied ($\mu = 16.3$ cm^{-1}).

Solution and Refinement of the Structure. The structure was solved by direct methods using MULTAN-78[28] to reveal the positions of the cobalt and copper atoms. Phasing on these atoms enabled the remainder of the nonhydrogen atoms to be located in subsequent structure factor calculations and difference Fourier maps. Hydrogen atoms for the imidazolate ring were directly located and included in the refinement as invariants with U fixed at 0.07 Å^2. Methyl hydrogens were set up and refined as rigid groups (C–H = 0.95 Å, H–C–H = 109.5°) pivoting on their respective carbon atoms. A common isotropic temperature factor for these hydrogens was refined to a final value of $U = 0.064\ (6)$ Å^2. Methylene hydrogens were placed in calculated positions (C–H = 0.95 Å) and refined with use of a riding model. A common isotropic temperature factor converged at $U = 0.074\ (10)$ Å^2. The ammonia moieties were initially set up and refined as rigid groups (N–H = 0.87 Å). In the final cycles of refinement the positional parameters of these hydrogen atoms were fixed and a common isotropic temperature factor converged at $U = 0.076\ (7)$ Å^2. Least-squares refinement was carried out in two blocks using SHELX-76.[28] In the first block (281 parameters) the scale factor and atoms of the cation, including perchlorate group 3, were refined while the second block (140 parameters) contained the scale factor and perchlorate groups 1, 2, and 4. All nonhydrogen atoms were refined anisotropically. The structure converged at $R_1 = 0.046$ and $R_2 = 0.065$[29] with no parameter shifting by more than 0.04 of its estimated standard deviation. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where

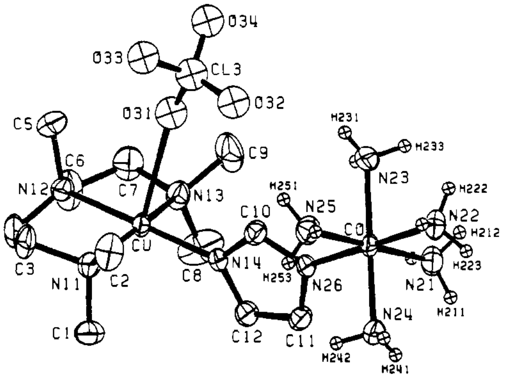

Figure 3. Structure of the $[(PMDT)Cu(im)Co(NH_3)_5]^{4+}$ cation showing the atom labeling scheme and the 40% probability thermal ellipsoids. Oxygen and chlorine atoms have been assigned arbitrarily as spheres with $B = 5.0$ Å^2 while hydrogen atoms are depicted as spheres with $B = 1.0$ Å^2.

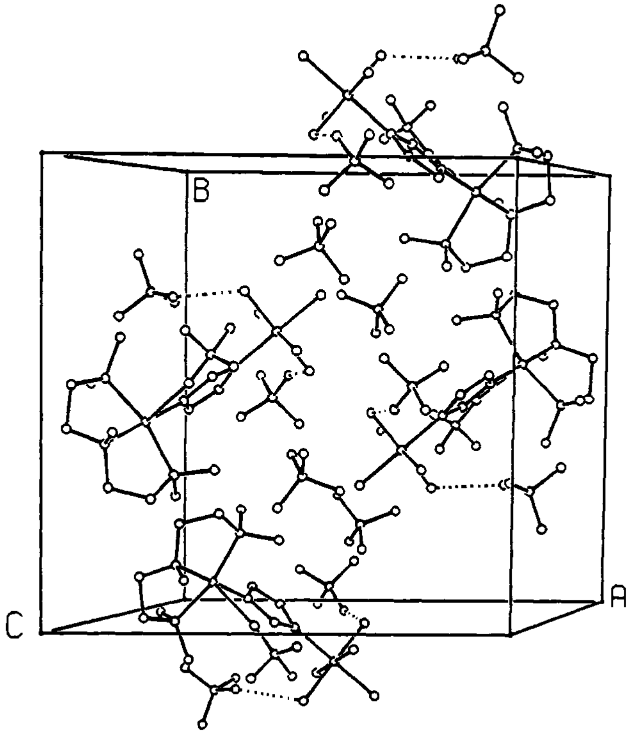

Figure 4. Unit cell packing of $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$. Dashed lines represent the hydrogen bonding interactions N(21)–H(211)···O(21) [O(21) is at $\bar{x}, \bar{y}, \bar{z}$] and N(25)–H(253)···O(43) [O(43) is at $x, -^1/_2 + y, {}^1/_2 - z$]. The N···O distances are 2.935 and 3.016 Å, O···H distances are 2.119 and 2.174 Å, and N–H–O angles are 152.4 and 164.9°, respectively. For clarity the unit cell outline has been translated by $-a/2$.

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(26) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379–3383.

(27) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I, p 99.

(28) Computing programs used in this work are MULTAN 78, a series of programs for direct-method phase determination by Main, Hull, Lessinger, Germain, Declercq, and Woolfson, SHELX-76, a crystallographic computing package by Sheldrick, and ORTEP II, the thermal ellipsoid plotting program by Johnson. All calculations were performed on a VAX-11/780 computer.

(29) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Final Nonhydrogen Atom Positional Parameters for $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$[a]

atom	x	y	z
Cu	−0.34516(5)	0.06135(5)	0.29355(6)
Co	−0.10296(6)	−0.13322(6)	0.14433(6)
Cℓ(1)	−0.05654(12)	0.18443(11)	0.10206(13)
Cℓ(2)	0.21341(11)	−0.01775(13)	0.21547(13)
Cℓ(3)	−0.13982(19)	−0.08591(14)	0.50759(16)
Cℓ(4)	0.43416(12)	0.28239(11)	0.52471(14)
O(11)	−0.1050(4)	0.1396(3)	0.0111(4)
O(12)	−0.0296(5)	0.1312(4)	0.1891(4)
O(13)	−0.1065(4)	0.2537(4)	0.1163(5)
O(14)	0.0246(4)	0.2160(5)	0.0913(5)
O(21)	0.1545(4)	0.0347(4)	0.1348(4)
O(22)	0.1586(4)	−0.0781(4)	0.2410(5)
O(23)	0.2643(4)	0.0308(4)	0.3009(4)
O(24)	0.2744(4)	−0.0610(4)	0.1781(5)
O(31)	−0.2014(7)	−0.0254(5)	0.4561(6)
O(32)	−0.1189(6)	−0.1405(5)	0.4420(5)
O(33)	−0.1781(11)	−0.1359(6)	0.5606(9)
O(34)	−0.0693(9)	−0.0625(11)	0.5836(13)
O(41)	0.4072(5)	0.3046(4)	0.6067(5)
O(42)	0.5034(4)	0.3359(4)	0.5181(6)
O(43)	0.3578(5)	0.2926(6)	0.4366(6)
O(44)	0.4656(5)	0.1997(4)	0.5353(6)
N(11)	−0.4435(4)	−0.0312(3)	0.2600(4)
N(12)	−0.4012(4)	0.1060(3)	0.3905(4)
N(13)	−0.2753(4)	0.1745(4)	0.3185(4)
N(14)	−0.2910(3)	0.0180(3)	0.1991(4)
N(21)	−0.0472(4)	−0.0473(4)	0.0857(4)
N(22)	−0.0072(4)	−0.2136(3)	0.1438(4)
N(23)	−0.0217(4)	−0.0934(4)	0.2820(4)
N(24)	−0.1816(4)	−0.1724(4)	0.0070(4)
N(25)	−0.1580(4)	−0.2206(4)	0.2024(4)
N(26)	−0.1962(3)	−0.0531(3)	0.1442(4)
C(1)	−0.5092(5)	−0.0180(6)	0.1534(5)
C(2)	−0.4072(6)	−0.1190(4)	0.2714(7)
C(3)	−0.4938(5)	−0.0184(5)	0.3302(6)
C(4)	−0.4971(5)	0.0759(5)	0.3511(6)
C(5)	−0.3495(6)	0.0789(7)	0.4999(5)
C(6)	−0.3959(6)	0.1986(5)	0.3841(7)
C(7)	−0.3017(6)	0.2222(5)	0.3945(7)
C(8)	−0.3007(8)	0.2230(6)	0.2237(7)
C(9)	−0.1747(5)	0.1608(6)	0.3592(8)
C(10)	−0.2216(5)	−0.0361(4)	0.2224(5)
C(11)	−0.2538(5)	−0.0050(4)	0.0645(5)
C(12)	−0.3105(4)	0.0382(4)	0.0992(5)

[a] Numbers in parentheses are errors in the last significant digit(s). Atoms are labeled as shown in Figure 3.

Table III. Interatomic Distances (Å) and Angles (Deg) for $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$[a]

Bond Distances			
Coordination Spheres			
Cu		Co	
Cu–N(11)	2.046(5)	Co–N(21)	1.957(7)
Cu–N(12)	2.012(5)	Co–N(22)	1.968(6)
Cu–N(13)	2.054(6)	Co–N(23)	1.983(5)
Cu–N(14)	1.954(6)	Co–N(24)	1.965(5)
Cu–O(31)	2.886(7)	Co–N(25)	1.961(7)
Cu···Co	5.859(2)	Co–N(26)	1.933(5)
Imidazolate Ring			
N(14)–C(10)	1.323(8)	C(11)–C(12)	1.35(1)
C(10)–N(26)	1.33(1)	C(12)–N(14)	1.363(9)
N(26)–C(11)	1.376(8)		
Bond Angles			
Coordination Spheres			
Cu		Co	
N(11)–Cu–O(31)	98.2(2)	N(21)–Co–N(22)	88.9(3)
N(12)–Cu–O(31)	92.1(2)	N(21)–Co–N(23)	88.3(2)
N(13)–Cu–O(31)	93.2(2)	N(21)–Co–N(24)	90.9(2)
N(14)–Cu–O(31)	88.0(2)	N(21)–Co–N(25)	179.2(3)
N(11)–Cu–N(12)	85.6(2)	N(21)–Co–N(26)	90.3(2)
N(11)–Cu–N(13)	165.2(2)	N(22)–Co–N(23)	89.8(2)
N(11)–Cu–N(14)	94.4(2)	N(22)–Co–N(24)	89.5(2)
N(12)–Cu–N(13)	85.5(3)	N(22)–Co–N(25)	90.3(3)
N(12)–Cu–N(14)	179.9(4)	N(22)–Co–N(26)	179.2(3)
N(13)–Cu–N(14)	94.6(3)	N(23)–Co–N(24)	179.0(3)
		N(23)–Co–N(25)	92.0(3)
		N(23)–Co–N(26)	90.1(2)
		N(24)–Co–N(25)	88.8(2)
		N(24)–Co–N(26)	90.6(2)
		N(25)–Co–N(26)	90.4(3)
Imidazolate Ring			
Cu–N(14)–C(10)	125.8(5)	Co–N(26)–C(10)	126.4(4)
Cu–N(14)–C(12)	129.6(4)	Co–N(26)–C(11)	128.7(5)
C(10)–N(14)–C(12)	104.5(6)	C(10)–N(26)–C(11)	104.9(6)
N(14)–C(12)–C(11)	109.6(6)	N(26)–C(11)–C(12)	107.5(6)
		N(14)–C(10)–N(26)	113.5(6)

[a] See Footnote *a* in Table II. Values are not corrected for thermal motion.

$w = 0.7593/[\sigma^2(F_o) + 0.00266F_o^2]$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 30. Hydrogen atom scattering factors came from a literature tabulation.[31] A final difference Fourier map showed no peak larger than 0.69 e Å^{-3}.

Final nonhydrogen atom positional parameters are given in Table II, and selected geometric information is summarized in Table III. Lists of final observed and calculated structure factor amplitudes, anisotropic thermal parameters, and hydrogen atom parameters are available as Tables S2–S4.[25] The structure of the cation is shown in Figure 3 together with the atom labeling scheme. Figure 4 displays a unit-cell packing diagram.

Discussion

Synthesis and Molecular Structure of $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$. The synthesis of the heterobinuclear Co(III)–Cu(II) complex was facilitated by the different kinetic properties of the $[(NH_3)_5Co(imH)]^{3+}$ and $[(PMDT)Cu(OH_2)]^{2+}$ cations. The former is kinetically inert and, upon addition of base, is readily converted[22] to $[(NH_3)_5Co(im)]^{2+}$ which reacts with the copper complex to form the desired imidazolate-bridged compound. A similar synthetic strategy was used to prepare *trans*-$[(NH_3)_5Co(im)Ru(NH_3)_4(SO_4)]^{3+}$.[19] It was also employed in the synthesis of an asymmetric imidazolate-bridged dicopper(II) complex in which the kinetic lability of the imidazolate ion on one of the two copper centers was controlled by its incorporation into a tetradentate chelating ligand.[17] Failure to control the reaction in such a manner leads to undesired symmetric complexes and to polymers.

The crystal structure consists of (μ-imidazolato)-(pentaamminecobalt(III))(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II) cations and perchlorate anions. Hydrogen bonding occurs between the hydrogen atoms of the coordinated ammonia molecules and the oxygen atoms of the perchlorate groups, as shown by the dashed lines in Figure 4.

The cation is comprised of a pseudooctahedrally coordinated cobalt(III) center connected to the $[(PMDT)Cu]^{2+}$ moiety by a bridging imidazolate ion. The average Co–NH$_3$ bond length of 1.967 (9) Å compares favorably with the average value of 1.959 (9) Å in $[(NH_3)_5CoNCCo(CN)_5]\cdot H_2O$ and with similar Co–N distances found in related complexes.[32] The Co–N(im) bond distance, 1.933 (5) Å, is slightly shorter as expected from charge considerations and from the sp^2 character of the nitrogen donor orbital. There is no obvious structural trans influence of the imidazolate ligand on the length of the cobalt–ammine bond opposite it in the coordination sphere. The plane of the imidazolate ring approximately bisects the N(23)–Co–N(25) and N(21)–Co–N(24) bond angles. The copper coordination sphere is a distorted square with a slight (±0.1 Å) D_{2d} distortion. The copper atom lies 0.085 Å above the mean plane through nitrogen atoms N(11)–N(14) on the side of the weakly coordinated perchlorate group [Cu–O =

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(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(31) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(32) Wang, B.-C.; Schaefer, W. P.; Marsh, R. E. *Inorg. Chem.* **1971**, *10*, 1492–1497.

2.886 (7) Å]. A similar geometry was observed for the $[(TMDT)_2Cu_2(im)(ClO_4)_2]^+$ cation except that the absence of the methyl group on the central nitrogen atom in the latter resulted in Cu–O(perchlorate) bonds ~0.4 Å shorter.[13a] Other features of the copper coordination geometry and the internal bond distances and angles of the ligands compare favorably with results of other X-ray studies of imidazolate bridged dicopper(II) complexes.[13,23]

Solid-State Magnetic and Spectroscopic Properties. The Curie law behavior, the value of 1.72 μ_B for the effective magnetic moment, and the ESR spectral parameters are typically those of an axially symmetric copper(II) center. The value of 386×10^{-6} cm^3 mol^{-1} for the TIP is somewhat greater than might be expected for the sum of the contributions from cobalt(III) and copper(II), 100×10^{-6} and 60×10^{-6} cm^3 mol^{-1}, respectively,[33] although values as high as 215×10^{-6} cm^3 mol^{-1} have been reported for cobalt(III) complexes.[34] The lack of hyperfine splitting from the cobalt(III) nucleus ($I = {}^7/_2$) in the frozen-solution ESR spectrum shows that little electron transfer from the copper to the cobalt occurs through the imidazolate-bridge orbitals. The absence of an intervalence charge-transfer band in the optical spectrum further supports this conclusion. The high potential for oxidizing copper(II) to copper(III) will provide an unfavorable barrier for this type of charge transfer in the $[(PMDT)Cu(im)Co(NH_3)_5]^{4+}$ cation.

Solution Behavior. The optical and ESR spectroscopic results demonstrate that the imidazolate bridge remains intact in acetonitrile and dimethyl sulfoxide solutions but that protons split the bridge according to eq 3. In protic solvents such as

$$[(PMDT)Cu(im)Co(NH_3)_5]^{4+} + H_3O^+ \rightleftharpoons [(NH_3)_5Co(imH)]^{3+} + [Cu(PMDT)(H_2O)]^{2+} \tag{3}$$

water the bridge is readily cleaved and eq 3 lies far to the right in millimolar solutions of the complex. Thus the potentiometric titrations are readily interpreted in terms of equilibria 4 and 5.

$$[(NH_3)_5Co(imH)]^{3+} + H_2O \xrightleftharpoons{K_1} [(NH_3)_5Co(im)]^{2+} + H_3O^+ \tag{4}$$

$$[Cu(PMDT)(H_2O)]^{2+} + H_2O \xrightleftharpoons{K_2} [Cu(PMDT)(OH)]^{+} + H_3O^+ \tag{5}$$

The value of K_1 agrees exactly with that reported previously[22] for the pentaammine(imidazole)cobalt(III) cation while the value of 8.75 for pK_2 compares favorably with the pK_a of 8.86 found for $[Cu(PMDT)(OH_2)]^{2+}$ in KNO_3 of 0.13 ionic strength.[35] As may be seen from Figure 2, however, the calculated and observed titration curves are not in exact agreement. The discrepancy occurs because neither the imidazolate-bridged complex (eq 3) nor removal of the PMDT ligand at low pH[35] was included in the theoretical analysis. Even with simplifying approximations,[35] a quartic equation results, and a more complete analysis was not attempted.

The imidazolate-bridged Co^{III}–im–Cu^{II} center is thus seen to be quite susceptible to hydrolysis in protic media but stable in nonprotic solvents. Reactions with anions and O_2^- will be interesting to monitor in the latter solvent systems as models for the active site of BESOD.

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Registry No. $[(PMDT)Cu(im)Co(NH_3)_5](ClO_4)_4$, 78279-94-4; $[Co(NH_3)_5(imH)](ClO_4)_3$, 15279-15-9; $[(PMDT)Cu(NCCH_3)_2](ClO_4)_2$, 74911-61-8.

Supplementary Material Available: Tables S1–S4 listing, respectively, temperature-dependent observed and calculated magnetic susceptibility data, final observed and calculated structure factors, nonhydrogen atom thermal parameters, and hydrogen atom positional parameters (17 pages). Ordering information is given on any current masthead page.

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(33) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry"; Interscience: New York, 1960; pp 421–422.

(34) Dodwad, S. S.; Datar, M. G. *Curr. Sci.* **1977**, *21*, 757–758.

(35) Allison, J. W.; Angelici, R. J. *Inorg. Chem.* **1971**, *10*, 2233–2238.