in these names are shown in Figure G (supplementary material). Further development of principles for naming di- and polynuclear coordination systems would permit naming more complex metallopolyboron hydrides by coordination nomenclature.[67]

Choice of System

In this report, and in the preceding paper,[2a] we have suggested several methods for describing both closed and nonclosed polyboron hydride structures and their hetero analogues (including metallo analogues). In many cases, two or more systems can be applied in naming the same polyboron hydride structure, even if we discount relatively minor variations within a system. For example, a closed metallopolyborane may be named on the basis of a parent polyborane using replacement prefixes, or it may be named by coordination nomenclature. A nonclosed metallopolyborane may be described by *nido* or *arachno* prefixes (where appropriate), by the "debor" method, by using a seco or cyclo prefix, or even by coordination nomenclature.

It has not been our purpose in these reports to recommend a preference for one system or another. Authors will certainly establish preferences as needed for different purposes. It has been our intent to introduce methods for describing unambiguous, structurally definitive names, not necessarily unique names.

Summary

In this report we have applied the methods for naming closed polyboron hydride systems developed in the preceding paper[2a] to nonclosed polyboron hydride systems, their hetero (including metallo) analogues, and derivatives. (1) We have suggested that the familiar descriptive prefixes *nido*- and *arachno*- can be used to describe certain nonclosed polyboron hydride structures, while at the same time caution was expressed about extended usage of these prefixes. (2) The "debor" method, briefly introduced into nomenclature rules for polyboron hydride systems,[3a] has been developed and applied in naming many nonclosed polyboron hydride structures. (3) The principles of the descriptor system for describing capped polyhedral systems developed in our earlier report[2a] have been extended to naming polyhedral fragments. (4) We have suggested that the prefixes "seco" and "cyclo", used to great advantage in organic nomenclature, be adapted for naming nonclosed polyboron hydride structures, especially where the debor system would require the creation of unusual closed polyhedral structures. (5) Finally, we have applied the principles described for nonclosed polyboron hydrides in naming metallopolyboron hydrides by coordination nomenclature.

Supplementary Material Available: Tables I–III, listing "debor" names for *nido*- and *arachno*-polyboron hydrides, "debor" and "descriptor" names for nonclosed polyboron hydrides, and "coordination" names for some nonclosed monometallopolyboron hydrides, Figures A–F, showing additional structures and names for nonclosed polyboron and heteropolyboron hydrides and closed metallopolyboron hydrides, and Figure G, showing ligand numberings for coordination names in Table III (12 pages). Ordering information is given on any current masthead page.

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(67) Development of coordination nomenclature for di- and polynuclear coordination systems is under study by various inorganic nomenclature groups.

Contribution from the Laboratoire de Chimie de Coordination du CNRS,
associé à l'Université Paul Sabatier, 31400 Toulouse, France

Coordination Sites of 5-Nitro-6-carboxyuracil: UV Study and X-ray Structure Determination of Diammine(5-nitroorotato)copper(II) Hydrate and Hexaamminebis(5-nitroorotato)tricopper(II) Pentahydrate

PHILIPPE ARRIZABALAGA, PAULE CASTAN,* and FRANÇOISE DAHAN

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A systematic study of UV spectra of 5-nitroorotic acid, for various pH values, shows that in the presence of metal ions (Cu(II)) the ligand is fully deprotonated. Two complexes, $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ (A) and $Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (B), have been prepared and investigated. Both complexes crystallize in the monoclinic system. Crystal data for A: space group $P2_1/c$, $a = 10.417$ (2) Å, $b = 7.212$ (1) Å, $c = 14.378$ (3) Å, $\beta = 94.30$ (2)°, $V = 1077.2$ Å^3, $Z = 4$, 1806 reflections, $R = 0.036$. Crystal data for B: space group $C2/c$, $a = 18.823$ (3) Å, $b = 7.329$ (1) Å, $c = 20.081$ (6) Å, $\beta = 105.33$ (2)°, $V = 2671.5$ Å^3, $Z = 4$, 2216 reflections, $R = 0.054$. These studies give the first evidence that an orotic acid derivative can coordinate the Cu^{2+} ion simultaneously by the two nitrogen sites of the completely deprotonated ligand.

Introduction

It has been largely demonstrated that orotic acids occupy a rather unique position in being the only effective precursor in the biosynthesis of pyrimidine bases of nucleic acids in living organisms. It is now established that during these processes the presence of metal ions is necessary,[1,2] particularly during the phosphoribosylation of orotic acids;[3] one of the roles played by the metal is making orotic acid available in the form of its reactive N(3)H dianion (Figure 1) where N(1) is unsubstituted, thus contributing to phosphoribosylation at the N(1) site. In this view, elucidation of metal ion effects on the pyrimidine nucleus could possibly lead to a better understanding of processes occurring in living systems.

Orotic acid is a potentially polydentate ligand, since coordination may occur through the two nitrogen atoms of the pyrimidine ring, the two carbonylic oxygens, and also the carboxyl group; moreover, the complexity of the pyrimidine system results from effects of pH changes and group substitutions on the ratio of tautomeric forms of HL^{2-}.

With this in mind, metal bonding studies (spectroscopic, potentiometric, etc.) have been carried out in aqueous solutions,[4-10] the determination of the crystal structures of the

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(1) Genchev, D. D. *Dokl. Bolg. Akad. Nauk* **1970**, *23*, 435.
(2) Lieberman, J.; Kornberg, A.; Simms, E. S. *J. Biol. Chem.* **1955**, *215*, 403.
(3) Victor, J.; Greenberg, L. B.; Sloan, D. L. *J. Biol. Chem.* **1979**, *254*, 2647.

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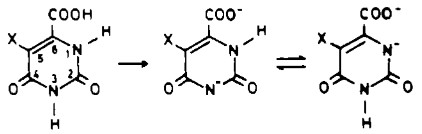

Figure 1. Tautomeric forms of the 5-substituted orotic acid dianion HL^{2-}: orotic acid, X = H; nitroorotic acid, X = NO_2.

metal complexes by X-ray diffraction often providing the ultimate decision. In this context, crystal data for two complexes of orotic acid have been recently published, i.e. diammine(orotato)copper(II)[11] and tetraaqua(orotato)nickel(II) hydrate;[12] in these two compounds the complexation specifically stabilizes the N(3)H tautomer and coordination to the metal occurs via one carboxylate oxygen and the nitrogen N(1) atom as chelation sites.

The situation is more complex for 5-nitroorotic acid, since the nitro group exhibits a strong influence on proton dissociation. Considering the pK_{a_1} and pK_{a_2} values for orotic acid (2.07 and 9.45)[13] and 5-nitroorotic acid (<1.5 and 4.94),[14] the low pK_{a_2} value for this last compound is due to negative inductive and resonance effects, which are working in the same direction to enhance the acidity. Therefore, the behavior of 5-nitroorotic acid toward metal ions is expected to be different from that of orotic acid itself.

For these reasons, the present studies were undertaken. A UV study of the systems formed by 5-nitroorotic acid with Ni(II) and Cu(II) was completed by an X-ray diffraction investigation of two copper(II) complexes: diammine(5-nitroorotato)copper(II) hydrate (A) and hexaamminebis(5-nitroorotato)tricopper(II) pentahydrate (B).

Experimental Section

Starting Materials. The potassium salt of 5-nitroorotic acid, orotic acid, and copper(II) chloride were obtained from commercial sources. Their purities were checked by chemical analysis and UV spectroscopy.

Reaction Procedures. Synthesis of B, $Cu_3(NH_3)_6(C_5N_3O_6)_2 \cdot 5H_2O$. $CuCl_2 \cdot 2H_2O$ (1.70 g, 10^{-2} mol) in 5 mL of water was added to a solution prepared by dissolving 2.39 g (10^{-2} mol) of the potassium salt of 5-nitroorotic acid in 100 mL of a 20% ethanol, 80% 12 M aqueous NH_4OH mixture. The resulting dark blue-violet solution was heated at 100 °C for 10 min and allowed to cool to room temperature. After 2 days the first complex precipitated as purple plates. This product was separated by filtration. Anal. Calcd for $C_{10}H_{28}Cu_3N_{12}O_{17}$: C, 15.41; H, 3.59; Cu, 24.47; N, 21.58. Found: C, 15.02; H, 3.48; Cu, 24.28; N, 21.65.

Synthesis of A, $Cu(NH_3)_2(C_5HN_3O_6) \cdot H_2O$. The intense blue filtrate collected after separation of compound B was left to stand in a flask. Some days after, new crystals occur as light blue plates. Anal. Calcd for $C_5H_9CuN_5O_7$: C, 19.07; H, 2.86; Cu, 20.19; N, 22.25. Found: C, 19.17; H, 2.73; Cu, 20.03; N, 22.21.

Synthesis of B′, $Cu_3(NH_3)_6(C_5N_3O_6)_2 \cdot 2H_2O$. From an aqueous solution of the complex B treated with acetone, a green amorphous precipitate was obtained. Anal. Calcd for $C_{10}H_{22}Cu_3N_{12}O_{14}$: C, 16.57; H, 3.03; Cu, 26.33; N, 23.20. Found: C, 16.30; H, 2.90; Cu, 25.59; N, 23.35.

Crystals of B (checked by chemical analysis and X-ray diffraction data) suitable for X-ray determination were grown by redissolving B′ in 5 M NH_4OH aqueous solution and allowing the solvent to slowly evaporate.

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Studies[a]

	$Cu(NH_3)_2(C_5HN_3O_6) \cdot H_2O$	$Cu_3(NH_3)_6(C_5N_3O_6)_2 \cdot 5H_2O$
	(a) Crystal Parameters at 20 °C[b]	
a, Å	10.417 (2)	18.823 (3)
b, Å	7.212 (1)	7.329 (1)
c, Å	14.378 (3)	20.081 (6)
β, deg	94.30 (2)	105.33 (2)
V, $Å^3$	1077.2	2671.5
cryst syst	monoclinic	monoclinic
absences	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$	hkl, $h + k = 2n + 1$ $h0l$, $l = 2n + 1$
space group	$P2_1/c$	$C2/c$
Z	4	4
ρ(calcd), g/cm^3	1.939	1.936
ρ(obsd),[c] g/cm^3	1.92	1.91
mol wt	314.55	778.64
F(000)	636	1580
	(b) Measurement of Intensity Data	
cryst dimens, mm	0.35 × 0.30 × 0.025	0.45 × 0.45 × 0.40
instrument	Nonius CAD4	Nonius CAD4
radiation	Mo $K\bar{\alpha}$ ($\bar{\lambda}$, 0.710 69 Å) graphite monochromatized	Mo $K\bar{\alpha}$ ($\bar{\lambda}$, 0.710 69 Å) graphite monochromatized
cryst–det dist, mm	210	210
det window		
height, mm	4	4
width, mm	4	4
take-off angle, deg	3.8	2.75
scan mode	ω–2θ	ω
scan range, deg	1.50 + 0.35 tan θ	1.20 + 0.35 tan θ
values determining the scan speed[d]		
SIGPRE	0.800	0.800
SIGMA	0.018	0.018
VPRE, deg/mn	6.7	10
TMAX, s	50	60
max 2θ, deg	56.6	60.5
stds		
intensity[e]	3 reflctns every 3600 s	3 reflctns every 7200 s
orientation	none	3 reflctns every 200 data reflctns
no. of indep reflctns collected	2669	3982
	(c) Treatment of Intensity Data	
reductn to F_o^2 and $\sigma(F_o^2)$	cor for bkgd, attenuators, and Lorentz-polarization in the usual manner[f]	
μ, cm^{-1}	20.7	24.7
transmission coeff		
T_{max}, T_{min}	0.95, 0.64	0.45, 0.33
obsd unique data, $\lvert F_o \rvert \geqslant 6\sigma(F_o)$, NO	1806	2216
no. of variables, NV	163	192
R_1[g]	0.036	0.054
R_2[h]	0.048	0.069
$w = 1/[\sigma^2(F_o) + (pF_o)^2]$, *p*	0.033	0.026

[a] All calculations were performed on an Iris 80 CII computer with use of local versions of SHELX 76, ORFLS, and ORFFE programs. [b] From a least-squares fitting of the setting angles of 25 reflections. [c] Flotation. [d] These parameters have been described: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, *B33*, 2639. [e] In both cases showed only random, statistical fluctuations. [f] Intensity data were corrected for absorption with use of the program AGNOST: Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035. [g] $R_1 = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$. [h] $R_2 = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$.

UV Spectroscopy. A Cary 14 recording spectrophotometer was employed for spectrophotometric measurements. In the ultraviolet light

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(4) Tucci, E. R.; Li, N. C. *J. Inorg. Nucl. Chem.* **1963**, *25*, 17.

(5) Davidenko, N. K.; Zinich, N. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 891.

(6) Dodin, G.; Dubois, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 3049.

(7) Tucci, E. R.; Ke, C. H.; Li, N. C. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1657.

(8) Sarpotdar, A.; Burr, J. G. *J. Inorg. Nucl. Chem.* **1979**, *41*, 549.

(9) Tucci, E. R.; Takahashi, F.; Tucci, V. A.; Li, N. C. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1263.

(10) Lalart, D.; Guillerez, J.; Dodin, G.; Dubois, J. E. *J. Chem. Soc., Perkin Trans, 2* **1981**, 1057.

(11) Mutikainen, I.; Lumme, P. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2233.

(12) Sabat, M.; Zglinska, D.; Jezowska-Trzebiatowska, B. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1187.

(13) Shugar, D.; Fox, J. J. *Biochim. Biophys. Acta* **1952**, *9*, 199.

(14) Tucci, E. R.; Doody, E.; Li, N. C. *J. Phys. Chem.* **1961**, *65*, 1570.

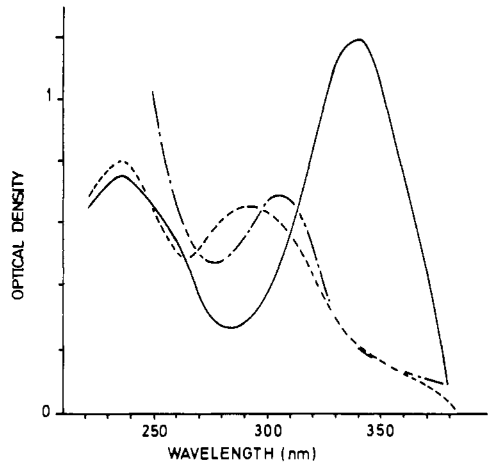

Figure 2. Ultraviolet absorption spectra at 20 °C of 10^{-4} M 5-nitroorotic acid: (- - -) in water (pH 2.5); (—) in aqueous NH_4OH solution (pH >7); (–·–·) after addition of 10^{-2} M Cu^{2+} ion (pH 7).

absorption studies, solutions of the orotic acid derivatives were diluted to 10^{-4} M concentration.

Each solution was adjusted to the desired pH by an Automatic Radiometer-Copenhagen titration chain using a 0.1 N aqueous NH_4OH solution. The absorption curves vs. pH are found in Figure 2.

Collection and Reduction of X-ray Data. $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ (A). The crystal used for the structure determination was a rectangular sky blue parallelepiped with the approximate dimensions reported in Table I. Details of the data collection and reduction are also given in Table I.

$Cu_3(NH_3)_6(C_5N_3O_6)\cdot 5H_2O$ (B). The crystal used in the diffraction study was a purple rhomb with dimensions as listed in Table I. Since the complex is not stable to the atmosphere in the solid state and recrystallizes to A in mother liquor, several attempts to obtain a single crystal were unsuccessful. The crystal for X-ray structure determination was grown in an ammoniacal solution and then sealed in this solution in a Lindemann glass capillary and rapidly mounted on the diffractometer. Details of data collection and reduction procedures appear in Table I.

Structure Solution and Refinement. (A) The structure was determined by the heavy-atom method. A Patterson map revealed the position of the copper atom. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms, which were refined anisotropically. The hydrogen atoms were located from a difference electron density map. Their geometry was idealized (N–H = 0.970 Å) except for those of the water molecule. They were introduced in the last cycles of refinement with the variations of their bonded atom with the equivalent U temperature factor of this last one increased by 0.015 $Å^2$. Neutral-atom scattering factors for non-hydrogen atoms and corrections for anomalous dispersion effects for copper were obtained from ref 15. Scattering factors for the hydrogen atoms were those of Stewart et al.[16]

The final full-matrix least-squares refinement converged at discrepancy values listed in Table I. The weighting scheme used in the minimization of the function $\sum w(F_o - |F_c|)^2$ is defined as $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$, where p is the factor to prevent overweighting of strong reflections. An analysis of variance according to F_o and $(\sin \theta)/\lambda$ showed satisfactory consistency. A final difference Fourier map showed no excursions of electron density greater than 0.50 e/$Å^3$.

(B) Analysis of normalized structure factors with parity groups[17] leads to the following values of $\langle |E|^2 \rangle$: 1.59 for l even, 0.36 for l odd. The extinction (hkl), $l = 2n + 1$, in space group $C2/c$ indicates atomic positions in a special position on an inversion center. One copper atom was placed at $^1/_2$, $^1/_2$, $^1/_2$.

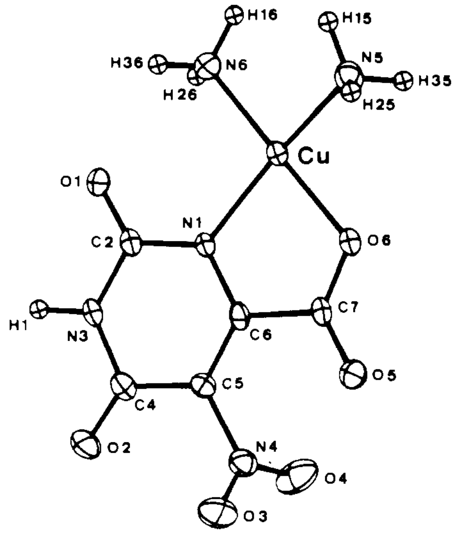

Figure 3. Perspective view of the diammine(5-nitroorotato)copper(II) molecule (A) with the atomic labeling scheme. The thermal ellipsoids are drawn at the 42% probability level. Hydrogen atoms are on an arbitrary scale.

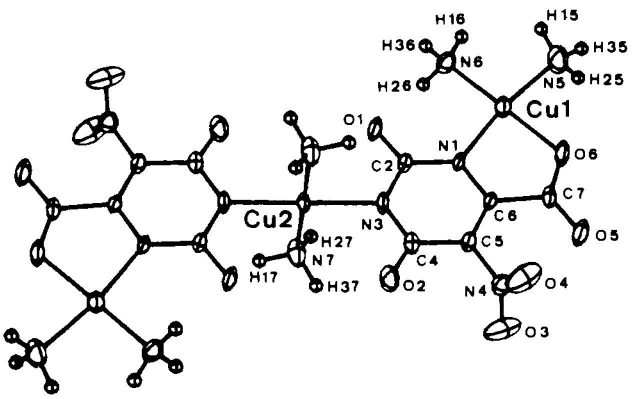

Figure 4. Perspective view of the hexaamminebis(5-nitroorotato)tricopper(II) molecule (B) with the atomic labeling scheme. The thermal ellipsoids are drawn at the 42% probability level. Hydrogen atoms are on an arbitrary scale.

Fourier maps revealed the other copper atom in a general position and then all non-hydrogen atoms. Except for the water molecules, the whole asymmetric unit is nearly in the same plane, explaining the normalization. All non-hydrogen atoms were refined anisotropically.

Refinement converged at values of the discrepancy indices given in Table I. An analysis of variance showed no unusual trends. The largest peaks on the final difference Fourier map were 1.4 and 1.2 e/$Å^3$ at 0.90 Å from the copper atoms, probably due to approximate absorption corrections.

The final atomic coordinates with their estimated standard deviations as derived from the inverse matrix of the last cycle of least-squares refinement are summarized for $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ and $Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ in Table II. Table IIS (supplementary material) contains the final thermal parameters with estimated standard deviations for these complexes. Views of the geometries of A and B along with the atom-labeling scheme are shown in Figures 3 and 4, respectively.

Results and Discussion

Interpretation of UV Spectra of HL^{2-}. Consideration of the UV spectra affords a clear distinction between the orotic acid dianion and the 5-nitroorotic acid homologue. For orotic acid, there is a very small shift (285 to 290 nm) to longer wavelengths when one moves from the acidic to the pH 12 region. If, in agreement with the results obtained by Dubois et al.[6] for 1-methylorotic acid and 3-methylorotic acid dianions,[8] we assume the absorbance at higher wavelengths to be only due

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(15) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72–79. Cromer, D. T. *Ibid.* Table 2.3.1, p 149.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. Y. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

Table II. Final Least-Squares Coordinates with Estimated Standard Deviations for $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ and $Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
$Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ (A)							
Cu	0.68272 (4)	0.70384 (7)	0.69755 (3)	O(6)	0.5333 (2)	0.5826 (4)	0.7492 (1)
N(1)	0.5551 (3)	0.7270 (4)	0.5853 (2)	N(5)	0.7927 (3)	0.5871 (5)	0.8006 (2)
C(2)	0.5735 (3)	0.8037 (5)	0.4996 (2)	N(6)	0.8307 (3)	0.8330 (5)	0.6473 (2)
N(3)	0.4731 (3)	0.7909 (5)	0.4317 (2)	OW	0.0170 (3)	0.6358 (6)	0.3235 (2)
C(4)	0.3514 (3)	0.7294 (5)	0.4423 (2)	H(1)	0.491 (0)	0.831 (0)	0.370 (0)
C(5)	0.3369 (3)	0.6637 (5)	0.5351 (2)	H(15)	0.882 (0)	0.622 (0)	0.796 (0)
C(6)	0.4386 (3)	0.6571 (5)	0.6002 (2)	H(25)	0.784 (0)	0.453 (0)	0.796 (0)
O(1)	0.6735 (2)	0.8810 (4)	0.4817 (2)	H(35)	0.765 (0)	0.629 (0)	0.860 (0)
O(2)	0.2677 (3)	0.7347 (5)	0.3781 (2)	H(16)	0.903 (0)	0.836 (0)	0.694 (0)
N(4)	0.2078 (3)	0.6033 (5)	0.5541 (2)	H(26)	0.806 (0)	0.959 (0)	0.630 (0)
O(3)	0.1618 (3)	0.4707 (5)	0.5119 (2)	H(36)	0.856 (0)	0.768 (0)	0.592 (0)
O(4)	0.1491 (3)	0.6930 (5)	0.6089 (3)	HW(1)	0.046 (0)	0.736 (0)	0.367 (0)
C(7)	0.4339 (3)	0.5606 (5)	0.6939 (2)	HW(2)	−0.030 (0)	0.555 (0)	0.362 (0)
O(5)	0.3400 (2)	0.4649 (4)	0.7077 (2)				
$Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (B)							
Cu(1)	0.17805 (3)	0.52938 (9)	0.36941 (3)	N(7)	0.5029 (2)	0.2292 (6)	0.5071 (3)
N(1)	0.2690 (2)	0.5025 (5)	0.4466 (2)	OW(1)	0.0807 (3)	0.6938 (8)	0.1667 (3)
C(2)	0.3410 (2)	0.5000 (6)	0.4448 (2)	OW(2)	0.5998 (3)	0.1907 (7)	0.6750 (3)
N(3)	0.3968 (2)	0.4961 (5)	0.5047 (2)	OW(3)	$^1/_2$	0.3302 (11)	$^3/_4$
C(4)	0.3840 (2)	0.4925 (7)	0.5682 (3)	H(15)	0.082 (0)	0.598 (0)	0.263 (0)
C(5)	0.3087 (2)	0.4889 (6)	0.5689 (2)	H(25)	0.060 (0)	0.693 (0)	0.326 (0)
C(6)	0.2544 (2)	0.4944 (6)	0.5088 (2)	H(35)	0.046 (0)	0.482 (0)	0.312 (0)
O(1)	0.3581 (2)	0.5009 (5)	0.3884 (2)	H(16)	0.181 (0)	0.514 (0)	0.247 (0)
O(2)	0.4362 (2)	0.4951 (6)	0.6210 (2)	H(26)	0.248 (0)	0.400 (0)	0.292 (0)
N(4)	0.2938 (2)	0.4845 (6)	0.6362 (2)	H(36)	0.253 (0)	0.615 (0)	0.289 (0)
O(3)	0.2986 (3)	0.3406 (6)	0.6662 (3)	H(17)	0.551 (0)	0.186 (0)	0.506 (0)
O(4)	0.2827 (3)	0.6247 (6)	0.6617 (3)	H(27)	0.466 (0)	0.178 (0)	0.469 (0)
C(7)	0.1728 (3)	0.4942 (7)	0.5056 (3)	H(37)	0.493 (0)	0.192 (0)	0.550 (0)
O(5)	0.1525 (2)	0.4672 (7)	0.5571 (2)	HW(11)	0.089 (0)	0.809 (0)	0.189 (0)
O(6)	0.1298 (2)	0.5174 (6)	0.4449 (2)	HW(21)	0.098 (0)	0.709 (0)	0.127 (0)
N(5)	0.0791 (3)	0.5824 (11)	0.3099 (3)	HW(12)	0.567 (0)	0.273 (0)	0.689 (0)
N(6)	0.2201 (3)	0.5125 (6)	0.2829 (2)	HW(22)	0.624 (0)	0.264 (0)	0.649 (0)
Cu(2)	$^1/_2$	$^1/_2$	$^1/_2$	HW(3)	0.473 (0)	0.410 (0)	0.715 (0)

to the N(3)H form, the orotic acid dianion may be in a predominant N(1)H form,[18] which would allow the formation of an intramolecular hydrogen bond between N(1)H and the carboxylate group. In contrast, the significant bathochromic changes observed for 5-nitroorotic acid near and below pK_{a_2} (from pH 7 to pH 12) strongly suggest that pK_{a_2} may be related, as for uracil itself,[19] to a N(1)H deprotonation. At this point, it is noteworthy that deprotonation of 3-methyluracil results in an appreciable bathochromic shift while deprotonation of 1-methyluracil causes a weak hypsochromic effect.[20]

Effect of Metal Cations. The bathochromic shift observed in the UV spectra of the orotic acid dianion upon addition of metal cations shows that, in this case, the N(3)H structure becomes favored; this assumption is further supported by X-ray structural determinations of copper(II)[11] and nickel(II)[12] orotato complexes, where the metal is chelated by N(1) and by one oxygen of the carboxylate. The case of the 5-nitroorotate dianion is not straightforward since different behaviors may be observed according to the nature of the metal cation. Thus, addition of Ni(II) to the aqueous nitroorotate dianion does not cause any changes in the spectra (λ_{max} = 340 nm), assuming that complexation occurs in the same way as in the orotate dianion itself, i.e. by N(1) and the carboxylate group; copper(II) addition then implies some curious changes in the ultraviolet absorption spectra as can be observed in Figure 2. At pH >7, the maximum wavelength in the presence of copper ions is 30 nm smaller than in the absence of metal.

It is reasonable to assume a uracil-like complexation mode for 5-nitroorotic acid in the presence of copper, the metal ion being more likely bonded to N(3); however, the strong residual absorbance beyond 300 nm suggests that, in water, both $N(1)^-$ and $N(3)^-$ are present. A tautomeric equilibrium shift has also been observed in uracil monoanions;[19,21] however, adding metal cations obviously favors the N(1)H structure. It is thus possible to assume that, in 5-nitroorotic acid anions, the occurrence of both carboxylate and nitro groups on the uracil nucleus makes the two nitrogen sites almost equivalent and offers the possibility of observing at the same time both orotic and uracil-like complexation models.

Copper Atom Coordination Spheres. The coordination spheres of the copper atoms are given in Figure 5 with the interatomic distances and their estimated standard deviations. Bond angles are listed in Table III, along with deviations of atoms from equatorial planes which are compared with those of diammine(orotato)copper(II)[11] and tetraaqua(orotato)nickel(II) hydrate,[12] called C and D, respectively, hereafter.

Copper atoms, denoted Cu in A and Cu(1) in B, are in a tetragonal coordination environment and are situated at the center of the plane defined by the deprotonated ring N(1), the carboxylate oxygen atom O(6), and the two ammonia atoms N(5) and N(6). The Cu–ligand lengths Cu–N(1) and Cu–O(6), 2.019 (3) and 1.978 (2) Å in A, 1.992 (4) and 1.964 (4) Å in B, agree well, within the limits of error, with those found in C, 2.005 (3) and 1.962 (3) Å, respectively. The bond angles indicate a distorted geometry because of the steric hindrance arising from coordination directly to a ring N atom and to the adjacent carboxylate O atom. The N–Cu–O angle is slightly more acute in A, 81.2 (1)°, than in B, 82.7 (1)°, and in C, 82.5 (1)°. Displacements from equatorial least-squares planes are very important, especially in A, contrary

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[18] Fox, J. J.; Yung, N.; Wempen, I. *Biochim. Biophys. Acta* **1957**, *23*, 295.

[19] Psoda, A.; Kazimierczuk, Z.; Shugar, D. *J. Am. Chem. Soc.* **1974**, *96*, 6832.

[20] Inagaki, K.; Kidani, Y. *Bioinorg. Chem.* **1978**, *9*, 175.

[21] Hathaway, B. J. *Struct. Bonding (Berlin)* **1973**, *14*, 49.

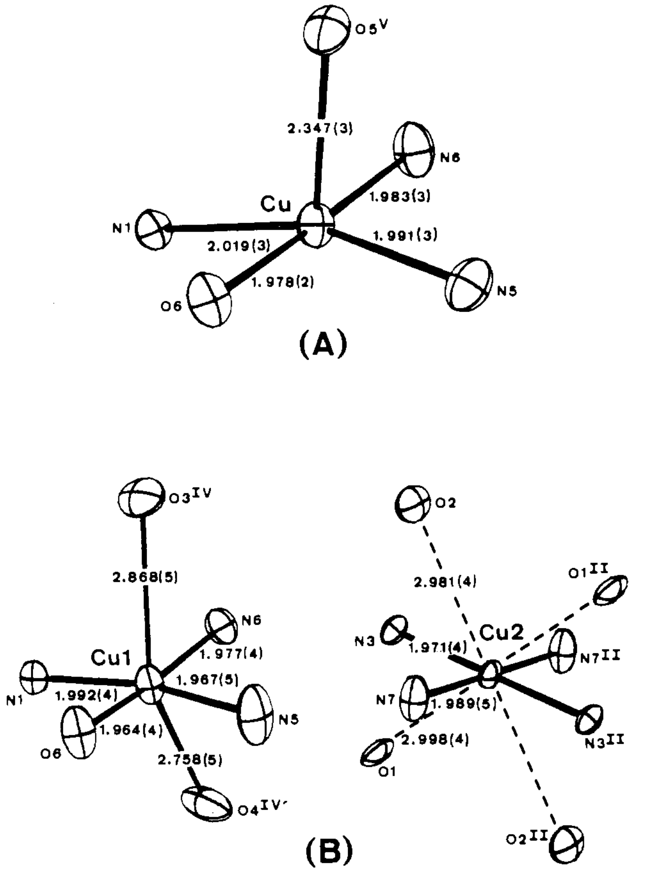

Figure 5. Environment about the Cu atoms in A and B. The distances (Å) are given with estimated standard deviations in parentheses. Roman superscript numbers indicate the following equivalent positions: in A, (V) $1 - x$, $^1/_2 + y$, $^3/_2 - z$; in B, (II) $1 - x$, $1 - y$, $1 - z$, (IV) $^1/_2 - x$, $^1/_2 - y$, $1 - z$, (IV′) $^1/_2 - x$, $^3/_2 - y$, $1 - z$.

Table III. Copper Atom Environments

(a) Bond Angles (deg) in the Coordination Sphere about Copper Atoms[a]

$Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ (A)			
N(5)–Cu–N(6)	92.9 (1)	N(6)–Cu–N(1)	98.8 (1)
N(5)–Cu–N(1)	159.6 (1)	N(6)–Cu–O(6)	178.2 (2)
N(5)–Cu–O(6)	87.6 (1)	N(1)–Cu–O(6)	81.2 (1)
N(5)–Cu–O(5^{V})	89.1 (1)	N(1)–Cu–O(5^{V})	108.0 (1)
N(6)–Cu–O(5^{V})	87.1 (1)	O(6)–Cu–O(5^{V})	91.2 (1)
$Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (B)			
N(5)–Cu(1)–N(6)	92.0 (2)	N(6)–Cu(1)–N(1)	100.5 (2)
N(5)–Cu(1)–N(1)	166.2 (2)	N(6)–Cu(1)–O(6)	172.8 (2)
N(5)–Cu(1)–O(6)	85.5 (2)	N(1)–Cu(1)–O(6)	82.7 (1)
N(5)–Cu(1)–O(3^{IV})	102.6 (3)	N(5)–Cu(1)–O($4^{IV'}$)	87.0 (2)
N(6)–Cu(1)–O(3^{IV})	67.5 (2)	N(6)–Cu(1)–O($4^{IV'}$)	71.6 (2)
N(1)–Cu(1)–O(3^{IV})	86.8 (2)	N(1)–Cu(1)–O($4^{IV'}$)	92.3 (2)
O(6)–Cu(1)–O(3^{IV})	106.4 (2)	O(6)–Cu(1)–O($4^{IV'}$)	115.0 (2)
O(3^{IV})–Cu(1)–O($4^{IV'}$) 138.1 (1)			
N(3)–Cu(2)–N(7)	89.4 (2)	N(3)–Cu(2)–N(3^{II})	180.0
N(3)–Cu(2)–N(7^{II})	90.6 (2)	N(7)–Cu(2)–N(7^{II})	180.0
N(3)–Cu(2)–O(1)	48.8 (1)	N(3)–Cu(2)–O(2)	49.2 (1)
N(7)–Cu(2)–O(1)	93.3 (2)	N(7)–Cu(2)–O(2)	86.5 (2)
N(3)–Cu(2)–O(1^{II})	131.2 (1)	N(3)–Cu(2)–O(2^{II})	130.8 (1)
N(7)–Cu(2)–O(1^{II})	86.7 (2)	N(7)–Cu(2)–O(2^{II})	93.5 (2)
O(1)–Cu(2)–O(2)	98.0 (1)	O(1)–Cu(2)–O(2^{II})	82.0 (2)
O(1)–Cu(2)–O(1^{II})	180.0	O(2)–Cu(2)–O(2^{II})	180.0

(b) Deviations (Å) of Individual Atoms from Equatorial Planes

Plane N(3), N(7), N(3^{II}), N(7^{II}) for B

O(1)	2.248 (4)	O(1^{II})	−2.248 (4)	Cu(2)	0.000
O(2)	−2.249 (4)	O(2^{II})	2.249 (4)		

Plane N(1), O(6),[b] N(5),[c] N(6)[d] (Comparison with C and D)

	A	B	C	D
N(1)	0.148 (3)	0.082 (5)	0.019	0.006
O(6)	−0.123 (3)	−0.063 (4)	−0.019	−0.006
N(5)	0.204 (4)	−0.186 (8)	0.022	−0.005
N(6)	−0.178 (3)	0.085 (5)	−0.024	0.005

A		B	
Cu	−0.1195 (4)	Cu(1)	−0.0293 (7)
O(5^{V})	−2.428 (3)	O(3^{IV})	−2.591 (5)
		O($4^{IV'}$)	2.651 (5)

C		D	
Cu	0.022	Ni	−0.0129
O(2^{I})	2.914	OW(6)	−2.106
O(2^{II})	−2.914	OW(7)	2.091

[a] Symmetry operations are as follows: in A, (V) $1 - x$, $^1/_2 + y$, $^3/_2 - z$; in B, (II) $1 - x$, $1 - y$, $1 - z$, (IV) $^1/_2 - x$, $^1/_2 - y$, $1 - z$, (IV′) $^1/_2 - x$, $^3/_2 - y$, $1 - z$. [b] O(4) in C, O(1) in D. [c] N(4) in C, OW(8) in D. [d] N(5) in C, OW(5) in D.

to the case for C and D. The primary coordination sphere could be described as a tetrahedrally distorted square plane around Cu in A and a distorted square plane with an evident tetrahedral component around Cu(1) in B.

The Cu(2) copper atom in B, being situated at an inversion site, is at the center of an almost ideal square plane defined by the deprotonated ring N(3) atom, the ammonia N(7) atom, and their two centrosymmetric mates. The N(3)–Cu(2)–N(7) angle, 89.4 (2)°, does not differ significantly from the ideal value of 90°. The Cu(2)–N(3) and Cu(2)–N(7) distances, 1.971 (4) and 1.989 (5) Å, respectively, are in the range of the expected values, but the Cu(2)–N(3) distance is slightly shorter than the Cu(1)–N(1) distance, 1.992 (4) Å, and significantly shorter than the Cu–N(1) distances in A and C, 2.019 (3) and 2.005 (3) Å, respectively.

Square-planar copper(II) has a decided tendency to extend its coordination sphere to five, the so-called (4+1)-coordination geometry, or to six, the (4+2)- and (4+1+1)-coordination geometries.[21] In A, the coordination sphere is extended to the (4+1) geometry by an intermolecular exo acid O(5) oxygen atom (Figure 5, Table III). The Cu–O(5) distance is short, 2.347 (3) Å, and can be compared with the bond distances of water or small anions occupying axial positions in copper(II) complexes.[22,23] The Cu–O(5) bond deviates from the ideal axial position, the largest deviation being 18°. The Cu atom lies 0.1195 (4) Å away from the equatorial plane of the pyramid, in the same direction as the axial atom O(5). Often, the axially coordinated atom is involved in a weak intramolecular interligand hydrogen bond,[24,25] enhancing the stability of the binding of the chelate. In this case, the acid O(5) atom is not involved in any hydrogen-bonding interaction. In contrast, the acid chelate atom O(6) is involved in a strong intermolecular hydrogen bond with the protonated N(3) ring atom: O(6)···N(3) = 2.891 (4) Å, H(1)···O(6) = 1.92 Å, N(3)–H(1)···O(6) = 177° (Table V).

In B, the Cu(1) coordination sphere is extended to a distorted-octahedral one with intermolecular nitro oxygen atoms at the apical positions (Figure 5, Table III). The Cu(1)–O(3) and Cu(1)–O(4) distances are rather long, 2.868 (5) and 2.758 (5) Å, respectively. They can be compared with those encountered in (glycylglycinato)(cytosine)copper(II),[23] 2.819 (3)

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[22] Hodgson, D. H. *Prog. Inorg. Chem.* **1977**, *23*, 211.

[23] Kistenmacher, T. J.; Szalda, D. J. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1659.

[24] Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

[25] Szalda, D. J.; Marzilli, L. G.; Kistenmacher, T. J. *Inorg. Chem.* **1975**, *14*, 2076.

Table IV. Pyrimidine Rings in A and B Compared with Those in Diammine(orotato)copper(II)[11] (C), Tetraaqua(orotato)nickel(II) Hydrate[12] (D), and Orotic Acid Hydrate[27] (E)

(a) Bond Lengths (Å)[a]

	A	B	C	D	E
N(1)–C(2)	1.378 (4)	1.366 (5)	1.372 (4)	1.359 (5)	1.363 (3)
C(2)–N(3)	1.380 (4)	1.373 (6)	1.384 (4)	1.368 (4)	1.373 (3)
N(3)–C(4)	1.363 (5)	1.359 (6)	1.368 (4)	1.376 (5)	1.369 (3)
C(4)–C(5)	1.435 (5)	1.421 (6)	1.440 (5)	1.432 (5)	1.433 (4)
C(5)–C(6)	1.361 (5)	1.359 (6)	1.358 (4)	1.339 (5)	1.346 (4)
C(6)–N(1)	1.346 (4)	1.350 (4)	1.362 (4)	1.356 (5)	1.365 (3)
C(2)–O(1)	1.226 (4)	1.257 (5)	1.232 (4)	1.241 (4)	1.227 (3)
C(4)–O(2)	1.221 (4)	1.241 (6)	1.241 (4)	1.246 (4)	1.237 (3)
C(6)–C(7)	1.521 (4)	1.520 (6)	1.526 (4)	1.523 (5)	1.498 (4)
C(7)–O(5)	1.225 (4)	1.209 (6)	1.227 (4)	1.241 (5)	1.197 (4)
C(7)–O(6)	1.267 (4)	1.284 (6)	1.285 (4)	1.256 (4)	1.306 (3)
N(3)–X[b]	0.970	1.971 (4)	0.84 (5)	0.96 (5)	0.89 (4)
C(5)–Y[c]	1.459 (4)	1.451 (6)	0.94 (5)	0.84 (5)	1.03 (3)
N(4)–O(3)	1.212 (4)	1.207 (6)			
N(4)–O(4)	1.219 (4)	1.192 (6)			

(b) Bond Angles (deg)[a]

	A	B	C	D	E
C(2)–N(1)–C(6)	118.7 (3)	118.1 (4)	117.9 (2)	118.3 (3)	122.7 (2)
N(1)–C(2)–N(3)	117.2 (3)	120.7 (4)	117.4 (3)	117.9 (3)	114.7 (2)
C(2)–N(3)–C(4)	127.3 (2)	122.6 (4)	126.5 (3)	125.8 (3)	126.4 (2)
N(3)–C(4)–C(5)	112.1 (3)	115.7 (4)	114.2 (3)	114.2 (3)	115.5 (2)
C(4)–C(5)–C(6)	121.4 (3)	120.6 (4)	118.2 (3)	118.7 (4)	119.0 (2)
C(5)–C(6)–N(1)	122.9 (3)	122.2 (4)	125.4 (3)	125.0 (4)	121.7 (2)
N(1)–C(2)–O(1)	123.3 (3)	121.1 (4)	124.4 (3)	122.8 (3)	124.1 (2)
N(3)–C(2)–O(1)	119.5 (3)	118.1 (4)	118.2 (3)	119.3 (3)	121.2 (2)
N(3)–C(4)–O(2)	121.5 (3)	120.2 (4)	120.6 (3)	119.8 (3)	119.5 (2)
C(5)–C(4)–O(2)	126.4 (3)	124.0 (5)	125.2 (3)	126.0 (4)	125.0 (2)
N(1)–C(6)–C(7)	113.6 (3)	114.3 (4)	113.9 (2)	113.3 (3)	114.1 (2)
C(5)–C(6)–C(7)	123.4 (3)	123.5 (4)	120.7 (3)	121.7 (4)	124.3 (2)
C(6)–C(7)–O(6)	114.8 (3)	114.6 (4)	114.6 (3)	116.3 (3)	114.1 (2)
C(6)–C(7)–O(5)	118.7 (3)	120.5 (5)	119.7 (3)	119.4 (3)	120.5 (2)
O(5)–C(7)–O(6)	126.4 (3)	124.9 (5)	125.7 (3)	124.3 (4)	125.4 (2)
C(2)–N(1)–Z[d]	128.4 (2)	129.4 (3)	129.6 (2)	127.9 (3)	117 (2)
C(6)–N(1)–Z[d]	113.0 (2)	112.4 (3)	112.3 (2)	113.6 (2)	121 (2)
C(2)–N(3)–X[b]	116.4	119.5 (3)	114 (3)	122 (3)	117 (2)
C(4)–N(3)–X[b]	116.4	117.9 (3)	119 (3)	112 (3)	116 (2)
C(4)–C(5)–Y[c]	115.8 (3)	116.6 (4)	120 (3)	119 (3)	117 (2)
C(6)–C(5)–Y[c]	122.8 (3)	122.8 (4)	122 (3)	122 (3)	124 (2)
C(7)–O(6)–Z[e]	116.7 (2)	115.8 (3)	116.5 (2)	116.7 (3)	105 (2)
C(5)–N(4)–O(3)	118.5 (3)	118.5 (4)			
C(5)–N(4)–O(4)	118.5 (3)	118.8 (4)			
O(3)–N(4)–O(4)	123.0 (3)	122.4 (5)			

(c) Deviations (Å) from the Least-Squares Planes Defined by the Six Atoms of the Pyrimidine Ring

	A	B	C	D	E
N(1)	0.007 (3)	−0.011 (4)	0.031 (3)	0.006	0.005
C(2)	−0.045 (4)	0.012 (5)	−0.022 (3)	−0.006	−0.018
N(3)	0.031 (3)	0.002 (4)	−0.014 (4)	−0.003	0.019
C(4)	0.001 (4)	−0.015 (5)	0.040 (4)	0.013	−0.005
C(5)	−0.038 (3)	0.008 (5)	−0.033 (3)	−0.014	−0.009
C(6)	0.029 (3)	0.006 (4)	−0.002 (4)	0.004	0.009
O(1)	−0.154 (3)	0.044 (4)	−0.078 (4)	−0.037	−0.043
O(2)	−0.005 (3)	−0.067 (4)	0.169 (4)	0.053	0.002
X[b]	0.11	−0.0186	−0.01	−0.03	0.02
Y[c]	−0.137 (3)	−0.006 (4)	−0.07	−0.08	0.04
C(7)	0.218 (3)	0.006 (4)	0.054 (3)	0.051	0.053
O(5)	0.485 (3)	0.168 (5)	−0.063 (3)	−0.007	0.039
O(6)	0.136 (3)	−0.125 (5)	0.234 (3)	0.160	0.100
Z[d]	0.0499 (5)	−0.1601 (7)	0.2870	0.1895	0.04
Z[e]					0.05
O(3)	0.777 (3)	1.029 (5)			
O(4)	−1.158 (3)	−1.050 (5)			

[a] The numbering is that of compounds A and B. [b] X = H(N3) for A, C, D, and E and Cu(2) for B. [c] Y = N(4) for A and B and H(C5) for C, D, and E. [d] Z = Cu for A and C, Cu(1) for B, Ni for D, and H(N1) for E. [e] As for footnote *d* except H(O6) for E.

Table V. Distances (Å) and Angles (deg) in the Interactions of the Type D–H···A

D[a]	H	A[b]	D–H	H···A	D···A	D–H···A
$Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ (A)						
N(3)	H(1)	$O(6^{III})$	0.97	1.92	2.891 (4)	177
N(5)	H(15)	$OW^{III''}$	0.97	2.26	3.073 (6)	141
N(5)	H(25)	$O(4^{V'})$	0.97	2.39	3.165 (5)	136
N(5)	H(35)	$O(1^{III'})$	0.97	2.06	2.976 (4)	158
N(6)	H(16)	$OW^{III''})$	0.97	2.14	3.082 (5)	163
N(6)	H(26)	$O(2^{II'})$	0.97	2.34	3.294 (4)	168
N(6)	H(36)	$O(3^{II})$	0.97	2.28	3.174 (5)	152
OW	HW(1)	O(2)	0.98	2.31	2.764 (4)	107
OW	HW(2)	$O(4^{II''})$	0.97	2.23	3.133 (5)	155
OW	HW(2)	$O(3^{II''})$	0.97	2.36	3.213 (5)	147
$Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (B)						
N(5)	H(15)	OW(1)	0.97	2.04	2.996 (8)	167
N(6)	H(16)	$OW(2^{IX})$	0.97	2.34	3.139 (7)	139
N(6)	H(26)	$O(3^{IV})$	0.97	2.23	2.790 (6)	116
N(6)	H(36)	$O(4^{IV'})$	0.97	2.32	2.841 (6)	113
N(7)	H(27)	$O(5^{IV})$	0.97	2.40	3.208 (6)	141
OW(1)	HW(21)	$O(5^{V})$	0.95	2.33	3.105 (7)	139
OW(1)	HW(21)	$O(1^{VIII'})$	0.95	2.34	2.879 (7)	115
OW(2)	HW(12)	OW(3)	0.95	2.02	2.887 (6)	150
OW(2)	HW(22)	$O(1^{II})$	0.95	1.94	2.809 (6)	150
OW(3)	HW(3)	O(2)	0.95	1.94	2.823 (5)	154

[a] Donor. [b] Acceptor with the following symmetry operations: no superscript in atom numbering, x, y, z; in A, (II) $1-x, 1-y, 1-z$, (II′) $1-x, 2-y, 1-z$, (II″) $-x, 1-y, 1-z$, (III) $x, {}^3/_2-y, -{}^1/_2+z$, (III′) $x, {}^3/_2-y, {}^1/_2+z$, (III″) $1+x, {}^3/_2-y, {}^1/_2+z$, (V′) $1-x, -{}^1/_2+y, {}^3/_2-z$; in B, (II) $1-x, 1-y, 1-z$, (III) ${}^1/_2+x, -{}^1/_2+y, z$, (IV) ${}^1/_2-x, {}^1/_2-y, 1-z$, (IV′) ${}^1/_2-x, {}^3/_2-y, 1-z$, (V) $x, 1-y, -{}^1/_2+z$, (VIII′) ${}^1/_2-x, {}^1/_2+y, {}^1/_2-z$, (IX) $-{}^1/_2+x, {}^1/_2-y, -{}^1/_2+z$.

and 2.713 (3) Å, with both intra- and intermolecular keto atoms. The Cu–nitro oxygen atom bonds are far from the ideal axial positions, the largest deviation being 25.0° (O(6)–Cu(1)–O(4) = 115.0 (2)°) and the O(3)–Cu(1)–O(4) angle having the value 138.1 (1)°. Nitro oxygen atoms are involved in weak hydrogen-bonding interactions with ammines (Table V). As noted by Kistenmacher et al.,[26] pyrimidine nitrogens have similar nucleophilicities and complexation could occur equally via N(1) or N(3), but coordination via N(1), which allows expansion of the coordination sphere of the copper, is favored whereas N(3) coordination leads to the blocking of both axial positions on the copper by the exocyclic keto oxygens. This situation is evident in A, but in B, as complexation must occur via N(1) and N(3), the Cu(2) secondary coordination sphere cannot be considered as blocked by keto atoms O(1) and O(2) but extended by them. There are four Cu–O weak interactions, two at 2.998 (4) Å and two at 2.981 (4) Å (Figure 5, Table III). The keto atoms are involved in strong hydrogen-bonding interactions with water molecules OW(2) and OW(3) (O(1)···OW(2) = 2.809 (6) Å, HW(22)···O(1) = 1.94 Å, OW(2)–HW(22)···O(1) = 150°: O(2)···OW(3) = 2.823 (6) Å, HW(3)···O(2) = 1.94 Å, OW(3)–HW(3)···O(2) = 154°) and in weaker hydrogen contacts with the water molecule OW(1) and ammonia molecules N(5) and N(6) (Table V). The pyrimidine ring is tilted at angles of 9.7, 6.0, and 84.1° to the respective equatorial planes of Cu in A and Cu(1) and Cu(2) in B, in agreement with the pseudocoordination of keto atoms to Cu(2) in B. In the two complexes A and B, the Cu–ammonia distances agree well with those observed in copper(II)–ammine compounds.[11,21,22]

Orotate Anion. Structural parameters of orotate anion in A and B are reported in Table IV, along with those of C, D, and the orotic acid monohydrate[27] E. Their comparison shows that the bond lengths appear to be rather similar, while the bond angles display some marked differences. The values of the C(2)–N(1)–C(6) angle are clearly smaller in A, B, C, and D, 4.0, 4.6, 4.8, and 4.0°, respectively, than in the orotic acid E, due to the complexation of N(1) to the metal. On the other hand, the N(1)–C(6)–C(5) angle is increased by 1.2, 0.5, 3.7, and 3.3° in A, B, C, and D, respectively, with regard to that in E, the smaller values in A and B being due to the nitro group at C(5) instead of hydrogen in C and D. This is also reflected in the values of the C(4)–C(5)–C(6) angle, 2.4 and 1.6° larger in A and B but 0.8 and 0.3° smaller in C and D compared to that in E. In the same way, angles involving N(3) show noticeable differences in B, due to the complexation to Cu(2). In all other compounds N(3) is protonated. The C═O bond lengths are quite similar in the same compound, but they are longer, on the borderline of experimental error, in B than in A, keto atoms in B having weak interactions with Cu(2). Nevertheless, this elongation does not influence significantly the C═O bond order. Deviations from least-squares planes through the six atoms of the pyrimidine ring (Table IV) reveal that the ring in compound A is not quite as planar as expected, the largest deviation being 0.045 (4) Å for C(2), which can be compared to that of 0.040 (4) Å for C(4) in C. Deviations of this magnitude are not uncommon for pyrimidine rings.[28] The exocyclic atoms are all significantly out of the ring plane in A, except the keto atom O(2) at 0.005 (3) Å. In B, Cu(2), N(4), and C(7) atoms are almost in the plane.

The carboxylate group is both twisted and bent in relation to the pyrimidine ring. Angles between the ring and the carboxylate group are 13.4, 7.9, 8.0, and 5° in A, B, C, and D, respectively. They differ by 15.6, 10.1, 10.2, and 7.2° from those observed in orotic acid E, due to the chelation of oxygen O(6) to the metal atom.

Influence of substitution of the proton at C(5) by a nitro group has been discussed above. Bond lengths and angles in the nitro group do not differ significantly in A and B. Angles between the nitro group and the pyrimidine ring planes have the respective values 65.5 and 98.5°, the latter being related to the pseudooctahedral coordination of copper atom Cu(1) in B with nitro oxygens at the apical positions.

Crystal Packing. In A, one of the principal features is the columnar packing of the square-pyramidal complex cations $Cu(NH_3)_2(C_5HN_3O_6)$ along the *c* axis. These columns are stabilized by the axial coordination of the O(5) atom to Cu. The overlap of the molecular π systems is similar to that found in molecular systems with extensive π networks,[28] and the distance of 3.40 Å between the stacking pyrimidine rings is also normal. The stability of the columns is further enhanced by the formation of an extensive intermolecular hydrogen bond system (Table V). Water molecules play the role both of acceptors from ammonia molecules and of donors to nitro oxygen atoms and to one keto atom. The strongest hydrogen bond occurs between N(3)H on the pyrimidine nucleus of one complex and the carboxylate O(6) atom of another molecule.

In B, the entities $Cu_3(NH_3)_6(C_5N_3O_6)_2$ form columns along the *a* axis with a larger distance of 3.58 Å between the stacking pyrimidine rings. The ammonia molecule N(7), coordinated to Cu(2), has only a weak hydrogen bond interaction, 2.40 Å, with a carboxylate O(5) atom. N(7) is enclosed in the Cu(2) coordination sphere, as are the keto atoms at the apex of the coordination polyhedron that increase the crystal stability with strong hydrogen bonds with water molecules. Ammonia molecules bound to Cu(1) are hydrogen bond donors to water molecules and nitro atoms. Details of hydrogen bonds are given in Table V.

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(26) Kistenmacher, T. J.; Sorrell, T.; Marzilli, L. G. *Inorg. Chem.* **1975**, *14*, 2479.

(27) Takusagawa, F.; Shimada, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2011.

(28) Voet, D.; Rich, A. *Prog. Nucleic Acid Res. Mol. Biol.* **1970**, *10*, 183.

The study of the complexation of 5-nitroorotic acid has been undertaken to gain further understanding of the important role played by metals in biochemical processes. In the present work we succeeded in isolating and determining the structure of a copper complex where both N(1) and N(3), as well as the carboxylate group, in a L^{3-} ligand are simultaneously involved as complexing sites. The UV study suggests that this complex exists also in solution. Consequently, the complexation site N(3) should not be neglected when biological processes are studied, as it might be stimulated either by the nature of the substituent on the pyrimidine ring or by the nature of the metal.

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Registry No. A, 85926-45-0; B, 85926-44-9; $Cu_3(NH_3)_6(C_5N_3O_6)_2$, 85955-86-8; 5-nitroorotic acid, 17687-24-0.

Supplementary Material Available: Listings of anisotropic thermal parameters for $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ and $Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (Table IIS), least-squares planes equations (Table VI), and observed and calculated structure factor amplitudes and projections of unit-cell contents for A and B (25 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, York University, Downsview (Toronto), Ontario, Canada M3J 1P3,
University of Kansas, Lawrence, Kansas 66045, and Canisius College, Buffalo, New York 14208

Crystallographic and Spectroscopic Studies of Low-Symmetry Nickel(II) Complexes Possessing Long Nickel–Nitrogen Bonds

A. B. P. LEVER,*[1] I. M. WALKER,*[1] P. J. McCARTHY,[2] K. B. MERTES,[3] A. JIRCITANO,[3] and R. SHELDON[3]

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The X-ray structure of bis(isothiocyanato)bis(*N*,*N*-diethylethylenediamine)nickel(II), $Ni[NH_2C_2H_4N(C_2H_5)_2]_2(NCS)_2$, is reported. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 10.438 (10) Å, b = 8.073 (8) Å, c = 14.876 (14) Å, α = 87.2 (8)°, β = 109.6 (7)°, γ = 112.8 (8)°, and Z = 2. The nickel complexes are six-coordinate and all-trans. There is significant rhombic distortion due to bent NiNCS coordination, short $NiNH_2$ bonds, and long $NiN(C_2H_5)_2$ bonds. The single-crystal polarized spectrum of this crystal at 10 K is reported and analyzed in terms of rhombic symmetry. Single-crystal spectroscopic data for $[Ni[NH_2CH_2CH_2N(C_2H_5)_2]_2(H_2O)_2]^{2+}Cl^-{}_2$ and $Ni[(CH_3)_2NCH_2CH_2N(CH_3)_2]_2(NCS)_2$ at 10 K are also reported. The data are compared with a range of other nickel complexes of low symmetry where both X-ray and spectroscopic data are available. The angular overlap model (AOM) is used, and it is demonstrated that AOM parameters in this low symmetry parallel those previously encountered for higher symmetries. In particular the use of sterically hindered amines provides a data set in which the Ni–N bond varies from about 208 to 233 pm. The σ-N AOM parameter is shown to correlate with the nickel–nitrogen bond length.

Introduction

In recent years we have extensively studied the electronic spectra of low-symmetry metal complexes, especially those of nickel(II) and cobalt(II).[4-11] In general, we have utilized the angular overlap model (AOM)[12] and the normalized spherical harmonic Hamiltonian (NSH) approach;[13] the utilities of these two approaches have recently been compared and contrasted.[11] In this paper we ask the question: how do the angular overlap parameters, specifically those relating to σ-bonding, depend upon the length of the metal ligand bond? Clearly, since the magnitudes of the AOM parameters depend directly upon the metal–ligand overlap integral,[12] they are generally expected to decrease as the bond lengthens, but prior to this study there has been no extensive experimental test of this prediction. Such a correlation can ultimately lead to an experimentally defined analytical relationship between these quantities.

When an asymmetrically *N*,*N*-disubstituted ethylenediamine is used as a ligand, the steric hindrance by the dialkylamino group is expected to prevent the nitrogen atom from approaching the nickel atom to the optimum distance. Since the early work of Goodgame,[14,15] a fairly extensive series of complexes of nickel, cobalt, and copper containing asymmetrically disubstituted ethylenediamines has been reported, and X-ray structures are available for several of them (see Table VI for summary). Indeed such complexes generally display a "normal" $M-NH_2$ bond length and a lengthened $M-NR_2$ bond length.

We have already reported the single-crystal spectra, at 10 K, of several of these complexes, and of control complexes containing symmetrically disubstituted ethylenediamines, and

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(1) York University.
(2) Canisius College.
(3) University of Kansas.
(4) A. B. P. Lever, G. London, and P. J. McCarthy, *Can. J. Chem.*, **55**, 3172 (1977).
(5) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, *Inorg. Chim. Acta*, **39**, 81 (1980).
(6) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, *Spectrosc. Lett.*, **12**, 739 (1979).
(7) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, *Inorg. Chim. Acta Lett.*, **44**, L143 (1980).
(8) I. M. Walker, A. B. P. Lever, and P. J. McCarthy, *Can. J. Chem.*, **58**, 823 (1980).
(9) L. Fabbrizzi, M. Micheloni, P. Paoletti, A. Poggi, and A. B. P. Lever, *J. Chem. Soc., Dalton Trans.*, 1438 (1981).
(10) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, *Can. J. Chem.*, **60**, 495 (1982).
(11) A. B. P. Lever, *Coord. Chem. Rev.*, **43**, 63 (1982).
(12) C. E. Schaffer, *Struct. Bonding (Berlin)* **5**, 68 (1968); **14**, 69 (1973).
(13) J. C. Donini, B. R. Hollebone and A. B. P. Lever, *Prog. Inorg. Chem.*, **22**, 225 (1977).
(14) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).
(15) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 5909 (1963).

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