laboratory that demonstrates that $N(SiMe_3)_3$ undergoes limited elimination chemistry with *B*-chloroborazenes.

Acknowledgment is made to Sandia National Laboratory, Contract 51-0623, for financial support of this research. We also acknowledge NSF Grants CHE-8007979, CHE-8201374, and DMB-8501824, which facilitated the purchases of the FTIR, high-field NMR spectrometers, and the VAX computer system.

Registry No. **1**, 17739-11-6; **1a**, 113110-92-2; **2**, 55718-76-8; **2a**, 113110-93-3; **2b**, 113110-94-4; **3**, 1870-71-9; **3a**, 113110-95-5; **3b**, 113132-30-2; $NaN(SiMe_3)_2$, 1070-89-9; $N(SiMe_3)_3$, 1586-73-8.

Supplementary Material Available: Tables S-2–S-4, listing hydrogen atom positional parameters, thermal parameters, and bond distances and angles (7 pages); Table S-1, listing observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Copper(II) and Nickel(II) Chelates of the Dihydrogen Nitrilotriacetate(1–) Ion: Crystal and Molecular Structure of Bis(*N*,*N*-bis(carboxymethyl)glycinato)copper(II) Dihydrate

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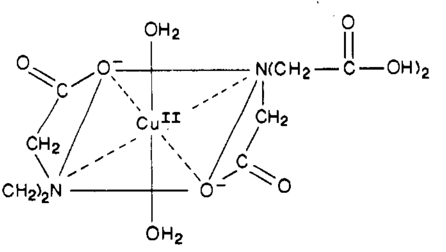
Bis(dihydrogen nitrilotriacetato) chelates of copper(II) and nickel(II) have been obtained as dihydrates, $[M(H_2NTA)_2]\cdot 2H_2O$ (M = Cu, Ni; H_3NTA = nitrilotriacetic acid or *N*,*N*-bis(carboxymethyl)glycine). The potentiometric and conductometric titration curves, TG–DTA analysis, spectral properties (IR, reflectance, ESR), and magnetic susceptibility data of these sparingly soluble in water compounds are discussed, taking in view the crystal structure of the copper complex $[Cu(H_2NTA)_2]\cdot 2H_2O$, which crystallizes in the monoclinic system, space group $P2_1/c$ ($a = 6.845$ (1) Å, $b = 14.095$ (4) Å, $c = 9.427$ (3) Å, $\beta = 91.95$ (2)°, $Z = 2$, $V = 909.1$ Å^3, $d_{\text{measd}} = 1.73$ (2) g·cm^{-3}, $d_{\text{exptl}} = 1.75$ g·cm^{-3}, $\mu = 1.631$ mm^{-1} (Mo Kα)). Final $R = 0.032$ and $R_w = 0.033$ for 1416 independent observed reflections. The copper atom lies in the center of symmetry. Two dihydrogen nitrilotriacetate(1–) or *N*,*N*-bis(carboxymethyl)glycinate(1–) ions, H_2NTA^-, act as tridentate chelating agents, making up an "all-trans" elongated octahedral coordination around the same copper atom (Cu–N = 2.062 (3) Å, Cu–O(3) = 1.954 (2) Å, Cu–O(13) = 2.321 (2) Å) where each ligand remains with a free carboxylic group of one of the two acetic or *N*-carboxymethyl arms. Two interesting structural features of this solid are (1) the very short trans-apical Cu–O(13) and Cu–O(13^i) bonds (symmetry code i: $1 - x$, $1 - y$, $1 - z$), as compared with the un-ionized carboxyl-to-copper(II) coordination bonds in related compounds (2.467–2.518 Å), and (2) the formation of hydrogen bonds O(14)–H···OW (2.598 (4) Å; 164°) involving one water oxygen atom and the carboxylic group of each ligand bonded to copper.

Introduction

During the last few years, the sodium salts of nitrilotriacetic acid (H_3NTA, H_3X) have been used as alternatives to polyphosphate in detergents, with a serious impact on heavy-metal remobilization in the environment.[2-5] In this regard, crystal structure determination of H_3NTA, Na_3NTA, $CaHNTA\cdot 2H_2O$, and several metal chelates such as $Na[Cu(NTA)]\cdot H_2O$[5] have been carried out. Divalent metal ions of Co, Ni, Cu, Zn, Pb, and Hg give water-soluble $M(HNTA)\cdot nH_2O$ acid chelates.[6] In addition, only copper[5-7] and nickel[6,7] form sparingly soluble $M(H_2NTA)_2\cdot 2H_2O$ solids. The two ν(C═O) absorption bands in the IR spectrum of $[Cu(H_2NTA)_2]\cdot 2H_2O$[5,6] and $[Ni(H_2NTA)_2]\cdot 2H_2O$[6] were assigned by Whitlow[5] and Rajabalee[6] to two uncoordinated carboxylic groups in the H_2NTA^- ligand. They then assumed that the dihydrogen nitrilotriacetate(1–) ion or *N*,*N*-bis(carboxymethyl)glycinate(1–) ion acts as a glycinate bidentate chelating agent, where the two water molecules probably complete an octahedral coordination around copper or nickel atoms (I). Our results also confirm the isolation of two acid forms of nitrilotriacetate complexes for Cu(II) and Ni(II), but the intensity ratio 2:1 of ν(C═O) IR absorption and the titration behavior against KOH in aqueous solution of the acid bis chelates are not in accord with this previous hypothesis. This paper deals with the properties of these complexes and the crystal structure of the copper chelate. The structure agrees well with the formula $[Cu(H_2NTA)_2]\cdot 2H_2O$ but does not confirm a bidentate role for the H_2NTA^- ion.[8]



I

Experimental Section

Synthesis of the Complexes. (a) (*N*,*N*-Bis(carboxymethyl)glycinato)copper(II) Dihydrate or Bis(dihydrogen nitrilotriacetato)copper(II) Dihydrate, $[Cu(H_2NTA)_2]\cdot 2H_2O$. This compound was obtained in aqueous medium by reaction of nitrilotriacetic acid ($H_3NTA = H_3X$, Sigma) and $Cu_2CO_3(OH)_2$ (Merck) in a 4:1 molar ratio. Thus, for

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0020-1669/88/1327-1227$01.50/0

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula: $CuC_{12}H_{20}N_2O_{14}$	$\beta = 91.95$ (2)°
$M_r = 479.84$	$V = 909.1$ Å^3
monoclinic space group: $P2_1/c$	$Z = 2$
$a = 6.845$ (1) Å	$d_{measd} = 1.73$ (2) g·cm^{-3}
$b = 14.095$ (4) Å	$d_{exptl} = 1.75$ g·cm^{-3}
$c = 9.427$ (3) Å	$\mu = 1.361$ mm^{-1} (Mo Kα)

scan type: ω–2θ with $s = 0.80 + 0.35 \tan\theta$
scan range: $1° < \theta < 35°$
octants collcd: $-9 < h < 9$; $0 \leqslant k \leqslant 19$; $0 \leqslant l \leqslant 13$
no. of indep rflns measd: 2354
final $R = 0.032$[a]
final $R_w = 0.033$[a]

[a] For 1416 independent observed reflections with $I > 3\sigma(I)$.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a]

	x	y	z	B_{eq}, Å^2
Cu	0.5	0.5	0.5	1.82
N	0.4417 (3)	0.4085 (2)	0.6640 (3)	1.5
C(1)	0.5403 (4)	0.3176 (2)	0.6303 (3)	1.9
C(2)	0.6664 (4)	0.3244 (2)	0.5012 (3)	1.9
O(3)	0.6508 (3)	0.3959 (2)	0.4216 (2)	2.3
O(4)	0.7732 (4)	0.2551 (2)	0.4791 (3)	3.0
C(11)	0.5219 (5)	0.4516 (2)	0.7969 (3)	2.1
C(12)	0.7069 (4)	0.5072 (3)	0.7721 (3)	2.2
O(13)	0.7651 (3)	0.5256 (2)	0.6553 (3)	2.8
O(14)	0.7946 (4)	0.5342 (2)	0.8902 (3)	3.8
C(21)	0.2273 (4)	0.3953 (2)	0.6688 (3)	2.0
C(22)	0.1630 (5)	0.3298 (2)	0.7862 (3)	2.0
O(23)	0.2681 (4)	0.2860 (2)	0.8654 (3)	3.2
O(24)	−0.0287 (3)	0.3298 (2)	0.7879 (3)	3.3
OW	1.1260 (4)	0.6138 (2)	0.8354 (3)	3.6

[a] Esd's are given in parentheses; $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\vec{a}_i\cdot\vec{a}_j$.

Table III. Bond Distances (Å) and Angles (deg)

Cu–O(3)	1.954 (2) [2][a]	C(2)–O(3)	1.259 (4)
Cu–N	2.062 (2) [2]	C(2)–O(4)	1.242 (4)
Cu–O(13)	2.321 (2) [2]	C(11)–C(12)	1.514 (4)
Cu–Cu^i	6.845 (1)	C(12)–O(13)	1.212 (4)
N–C(1)	1.487 (4)	C(12)–O(14)	1.303 (4)
N–C(11)	1.481 (4)	C(21)–C(22)	1.518 (4)
N–C(21)	1.481 (4)	C(22)–O(23)	1.192 (4)
C(1)–C(2)	1.519 (4)	C(22)–O(24)	1.313 (4)
O(3)–Cu–O(3^i)	180	C(1)–C(2)–O(4)	116.1 (3)
O(3)–Cu–N	86.11 (9)	O(3)–C(2)–O(4)	124.6 (3)
O(3)–Cu–O(13)	86.8 (1)	Cu–O(3)–C(2)	114.2 (2)
N–Cu–O(13)	77.97 (9)	N–C(11)–C(12)	111.7 (2)
Cu–N–C(1)	106.1 (2)	C(11)–C(12)–O(13)	123.6 (3)
Cu–N–C(11)	107.6 (2)	C(11)–C(12)–O(14)	112.5 (3)
Cu–N–C(21)	108.6 (2)	O(13)–C(12)–O(14)	123.9 (3)
C(1)–N–C(11)	112.6 (2)	Cu–O(13)–C(12)	105.4 (2)
C(1)–N–C(21)	110.8 (2)	N–C(21)–C(22)	114.3 (3)
C(11)–N–C(21)	111.4 (2)	C(21)–C(22)–O(23)	126.0 (3)
N–C(1)–C(2)	113.1 (2)	C(21)–C(22)–O(24)	108.9 (3)
C(1)–C(2)–O(3)	119.3 (3)	O(23)–C(22)–O(24)	125.1 (3)

[a] Numbers in brackets give the multiplicity.

example, to 26.16 mmol of H_3NTA in 400 mL of water was slowly added 6.54 mmol of $Cu_2CO_3(OH)_2$, the reaction mixture gently heated ($t < 60$ °C) and stirred, and the CO_2 (byproduct) removed with vacuum. The clear blue solution was cooled and filtered to remove any insoluble material and then evaporated at room temperature in a crystallizing flask, where a pale blue powder or crystals of the desired product were obtained in good yield (>5.6 g, >90%). This starting material was recrystallized from excess hot water to give many sky blue hexagonal prism crystals, most of them being double or twinned. This sparingly water-soluble product was filtered off, washed with cold water and ethanol, and air-dried. Anal. Calcd for $C_{12}H_{20}CuN_2O_{14}$: C, 30.04; H, 4.20; N, 5.84; Cu, 13.24. Found: C, 29.56; H, 4.02; N, 5.64; Cu, 13.8 ± 1 (complexometry). The product loses two molecules of water at t = 393–443 K. Alternative syntheses were described by Rajabalee.[6] Copper(II) also forms $Cu(HNTA)\cdot2H_2O$ as pale-blue sheets or needle crystals[6,7].

(b) (*N*,*N*-Bis(carboxymethyl)glycinato)nickel(II) Dihydrate or Bis(dihydrogen nitrilotriacetato)nickel(II) Dihydrate, $[Ni(H_2NTA)_2]\cdot2H_2O$. This complex was easily prepared by a procedure analogous to that for the copper solid, by reacting nitrilotriacetic acid and $NiCO_3\cdot2Ni(OH)_2\cdot4H_2O$ (Merck) (in the molar ratio 6:1). This gives a pale bluish violet powder, very insoluble in water at room temperature, which can only be purified by leaching with boiling water. No crystals of this product were available. Anal. Calcd for $C_{12}H_{20}N_2NiO_{14}$: C, 30.34; H, 4.24; N, 5.90; Ni, 12.36. Found: C, 30.28; H, 4.20; N, 5.81; Ni 13 ± 1. The two water molecules are lost at 413–448 K. The yield is usually very high (>90%) with a small amount of $Ni(HNTA)\cdot3H_2O$ as a byproduct (green).[6,7]

By reaction of H_3NTA and the appropriate metal(II) carbonate or metal(II) hydroxycarbonate (M = Co, Zn, Cd, Pb) (in acid-to-metal molar ratio 2:1), it should be possible to obtain a solution of the hypothetical compound $[M(H_2NTA)_2]$, but in these cases, precipitation occurs with disproportionation to equimolar amounts of H_3NTA and $[M(HNTA)]\cdot nH_2O$.[7]

X-ray Structure Determination. Diffraction data for $[Cu(H_2NTA)_2]\cdot2H_2O$ were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The blue single crystals were shaped as parallelepipeds with dimensions 0.25 × 0.18 × 0.15 µm.[3] Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit of 25 reflections in the range $5.2 < \theta < 17.8°$. The intensities of three standard reflections measured every 90 min showed no systematic variation. Intensities were corrected for Lorentz and polarization effects. Absorption correction was not necessary. No extinction correction was performed. Direct methods[9] (MULTAN 80) were used to solve the structure, by locating the copper atoms. Carbon, nitrogen, and oxygen atoms were found by direct methods or by Fourier and difference Fourier synthesis. The structure was then refined by full-matrix least-squares methods[10] to final residuals $R_F = 0.032$ and $R_{wF} = 0.033$, with $w = 1/\sigma^2(F)$, minimizing the function $\sum_{hkl}w_{hkl}(|F_o| - |kF_c|)^2$. H atoms could be located from difference maps but were not refined and were assigned isotropic thermal parameters 1 Å higher than the isotropic factor of the corresponding C or N atom. Final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. All calculations were performed with the local system of programs adapted for the UNIVAC 1110 computer.[11]

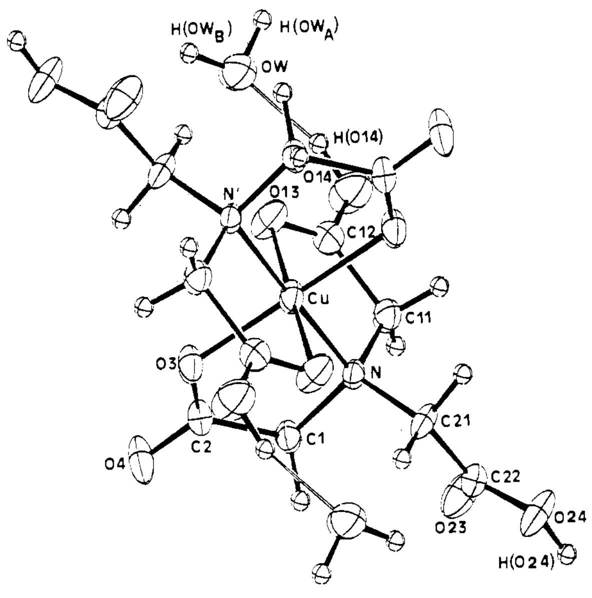

Figure 1. ORTEP view of the copper(II) complex $[Cu(H_2NTA)_2]\cdot2H_2O$.

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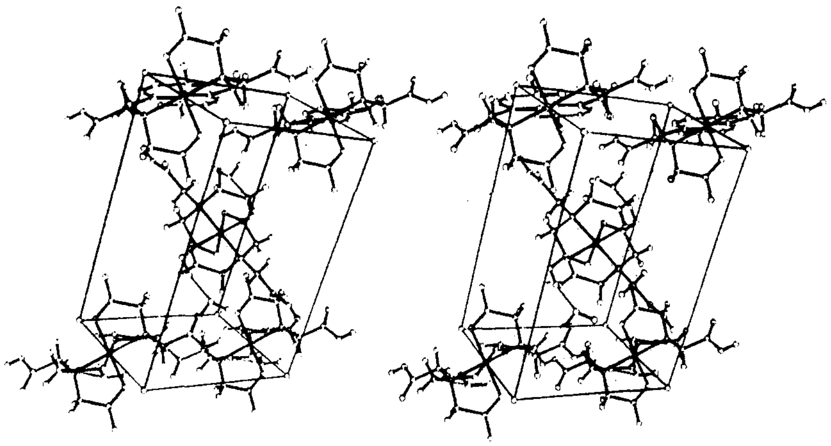

Figure 2. ORTEP stereoscopic view of the unit cell of $[Cu(H_2NTA)_2]\cdot 2H_2O$.

Scattering factors and the anomalous dispersion correction terms were taken from ref 12. The highest peak in the last difference Fourier map at the end of the refinement was less than 0.1 $e\cdot Å^{-3}$. Tables of anisotropic thermal parameters, positional parameters for the hydrogen atoms, C–H and O–H distances, distances from the atoms to the mean planes, torsion and dihedral angles, van der Waals distances, and structure factors have been deposited as supplementary material.

Physical Measurements. Potentiometric and conductometric titration curves, TG and DTA diagrams, IR, near-IR–vis–UV, and ESR spectra and magnetic susceptibility data of the studied complexes were obtained as described in ref 13 for the solid-state derivative $[Cu(HNPDA)(H_2O)]$ of *N*-(2-carboxyethyl)iminodiacetic acid (H_3NPDA).

Results and Discussion

Description of the Structure. Bonds lenghts and angles are given in Table III. An ORTEP drawing of the complex is given in Figure 1 and specifies the labeling scheme in the asymmetric unit. Figure 2 represents a stereoscopic view of the cell.

Copper Coordination. The copper atom is in the center of symmetry in the (2b) position of the space group. It is chelated by two H_2NTA^- ligands in their tridentate form; in each ligand, the nitrogen atom, the oxygen atom O(3) of the acetate group, and the atom O(13) of one of the two acetic groups are involved. The other acetic group (C(21)–C(22)–O(23)–O(24)) is not involved in the coordination of the copper. Therefore, the copper is hexacoordinated: the square base consists of the atoms N, N^i, O(3), and $O(3^i)$ (symmetry code i: $1 - x$, $1 - y$, $1 - z$). The shortest Cu–O(3) distance is close to those observed in $[Cu(HNPDA)(H_2O)]$[13] (averaged value 1.967 (3) Å) or in $Na[Cu(NTA)]\cdot H_2O$[5] (1.950 (4) Å). The Cu–N distance is comparable with that observed in this last compound (2.086 (5) Å) in spite of the greater deformation of the square base. Indeed, in the $[Cu(H_2NTA)_2]\cdot 2H_2O$ complex, the position of the copper atom, at the center of symmetry, induces a perfectly square base; in addition, the angles formed by the diagonal directions are fairly close to 90°. The apical positions of the octahedron are occupied by the atoms O(13) and $O(13^i)$. It is interesting to note the very short distances Cu–O(13) and Cu–$O(13^i)$ in the trans-apical carboxylic-group-to-copper coordination, in comparison with the longer (–COOH)–Cu bonds formed in related compounds: 2.467 Å in the derivative $[Cu(H_2EDTA)(H_2O)]$[14] of ethylenediaminetetraacetic acid (H_4EDTA), 2.488 Å in the derivative $[Cu(HNPDA)(H_2O)]$[13] and 2.518 Å in the derivative $[Cu(H_3DTPA)]\cdot H_2O$[15] of diethylenetriaminepentaacetic acid (H_5DTPA). The lengthening direction in the octahedron O(13)–Cu–$O(13^i)$ forms an angle of 12.3° with the normal to the plane of the square base.

Conformation of the Ligand. The internal geometry of the H_2NTA^- ligand is in good agreement with the bond lengths C—C, C=O, and C—N given in the literature. In particular, the longest distances C(12)–O(14) and C(22)–O(24) correspond to single bonds of the type C–(OH), whereas the shortest distances C(12)–O(13) and C(22)–O(23) correspond to double-bonded C=O carboxylic groups. Finally, the bonds C(2)–O(3) and C(2)–O(4), of similar length, lying between the two previous types of bonds, have a partial double-bond character because of the delocalization of the π electrons of the carboxylate groups O(3)–C(2)–O(4). The charge transfer of the O(3) atom toward the copper atom leads to a lengthening of the C(2)–O(3) bond, in relation to C(2)–O(4), and also of the C(12)–O(13) bond, in relation to C(22)–O(23). The chelation of the copper by the two H_2NTA^- groups leads to the formation, for each ligand, of two five-membered rings with a common edge (Cu–N or Cu–N^i). This centrosymmetric and fairly regular arrangement shows a clear difference from that found in $Na[Cu(NTA)]\cdot H_2O$[5] in which the NTA^{3-} ligand plays an overall hexadentate role, responsible for the large distortion in the octahedron around each copper atom. If we consider the chelate ring A formed by the acetate arm Cu, N, C(1), C(2), O(3), the O(3) and O(4) atoms of the carboxylate groups lie on either side of the mean plane Cu, N, C(1), C(2) of this chelate ring, for which the maximum deviation from the mean plane remains less than 0.05 Å. On the other hand, because of the "gauche" ring B conformation (Cu, N, C(11), C(12), O(13)), the calculation of a mean plane was not carried out. Moreover, the dihedral angle formed by the plane O(13), Cu, N and the mean plane of ring A is 93.65°. Finally, the third arm (N, C(21), C(22), O(23), O(24)) does not constitute a ring but the conformation of the bonds Cu–N–C(21)–C(22) does not deviate significantly from the planarity according to the χ^2 value (7.3): the atoms O(23) and O(24) are found on either side of the mean plane (supplementary material).

The different conformations of the H_2NTA^- ligand in its metal chelates can be described either by the endocyclic torsion angles around the N–C and C–C bonds in each of the three arms or by the dihedral angles formed between each NCC plane and the COO groups (supplementary material). Our results also show the very different conformations of the chains of bonds Cu–N–C(1)–C(2) and Cu–N–C(11)–C(12).

Crystal Packing. The asymmetric unit contains, in addition, one water molecule $H_2(OW)$, which is not coordinated to the copper atom but is linked to the complex by three hydrogen bonds:

	dist, Å	angle, deg
O(14)–H(O14)···OW	2.598 (4)	164
OW–HA(OW)···$O(4^{ii})$	2.723 (3)	176
OW–HB(OW)···$O(3^{iii})$	2.911 (3)	150

symmetry codes: (ii) $2 - x$, $^1/_2 + y$, $^3/_2 - z$; (iii) $2 - x$, $1 - y$, $1 - z$

In addition, the crystalline cohesion is ensured by a fourth hydrogen bond between two homologous complexes related by the *c* glide plane: O(24)–H(O24)···$O(4^{iv})$, 2.586 (3) Å, 158° (symmetry code iv: $-1 + x$, $^1/_2 - y$, $^1/2 + z$).

It is interesting to note the binding of the oxygen atoms of water molecules to the protons on the carboxylic groups bonded to

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(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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copper, giving rather short hydrogen bonds. This leads to discrete units $[Cu(H_2NTA)_2]\cdot 2H_2O$ of the complex, connected together by a network of six hydrogen bonds per unit (in which the two water molecules participate). Among the several van der Waals bonds that contribute to the cohesion of different complexes, the shortest (3.087 (5) Å) implies the C(12) and $O(24^v)$ atoms (symmetry code v: $1 + x, y, z$). The X-ray study enables us to determine the copper atom environment unambiguously. It shows the tridentate role played by the H_2NTA^- ligand in the copper coordination sphere and proves also that the water molecules are not directly involved. This differs from the idea[5] proposed from the results of infrared spectra, where the water molecules were expected to be directly bonded to the copper atom.

Properties of the Complexes $[M(H_2X)_2]\cdot 2H_2O$ (M = Cu, Ni). Solution Properties. The potentiometric and conductometric titrations of aqueous solutions (ca. 1×10^{-3} M) of $[M(H_2X)_2]\cdot 2H_2O$ (M = Cu (Figure 4, supplementary material), Ni) against KOH (0.1 M) are very similar. Both titrations show two independent steps, which take place in acid and alkaline media and involve 3 and 1 equiv of base/mol of complex, respectively.

Among the four carboxylic functions, the two coordinated to the copper exhibit a greater acidity than the two nonbonded ones. However, it is expected that the small difference in their pK_a values is not sufficient enough to observe a two-step neutralization process, in which 2 equiv of base/mol of complex is involved in each step.

Actually, it is well-known that the titrations of the metal-bonded and the free carboxylic groups of the related compounds $[M(H_2EDTA)(H_2O)]$ (M = Cu,[14] Ni) take place as overlapped equilibria in acid media. The observed titration pattern of $M(H_2X)_2$ is not in accordance with the above prediction.

The titrations of the complexes $M(H_2X)_2$ (M = Cu, Ni) in solution would be consistent with the equilibria

$$M(H_2X)_2 + 3OH^- \rightleftharpoons M(X)^- + HX^{2-} + 3H_2O \qquad (I)$$

$$M(X)^- + HX^{2-} + OH^- \rightleftharpoons M(X)_2^{4-} + H_2O \qquad (II)$$

Equilibrium I supposes that the hypothetical intermediate species $[M(X)(HX)]^{3-}$ would be less stable than the corresponding equimolar mixture of $M(X)^-$ (log K = 11.26 and 12.68 for M = Cu and Ni) and HX^{2-} ($pK_a = pK_3(H_3X) = 9.73$). Note that, to be titrated in alkaline medium, the species $[M(X)(HX)]^{3-}$ would have the proton on the nitrogen atom of the coordinated ligand HX^{2-}. That seems improbable with M = Cu or Ni, but it is indeed acceptable for the free ligand species HX^{2-}.

Equilibrium II is consistent with the knowledge on the salt $K_4[Ni(X)_2]\cdot 8H_2O$ in the solid state.[16]

With other divalent metal ions M(II) (such as M = Co, Zn, Cd, Pb, or Hg) it is possible to prepare solutions of apparent $M(H_2X)_2/H_2O$ systems, but all these lead to disproportionation to H_3X and $M(HX)\cdot nH_2O$ solids.[7] It seems that only Cu(II) and Ni(II) form complexes stable enough with H_2X^- to allow the isolation of $[M(H_2X)_2]\cdot 2H_2O$.[6,7]

Thermal Stability. The solid-state species $[M(H_2X)_2]\cdot 2H_2O$ (M = Cu, Ni; Figure 5, supplementary material) have similar TG and DTA diagrams. In both cases, the first step shows the loss of the two water molecules (at 393–443 K for the Cu complex and 413–448 K for the Ni complex) and the pyrolytic decomposition of the organic ligand (at 473–673 K for Cu and 498–673 K for Ni solid-state species) and gives CuO and probably $NiCO_3\cdot NiO$. It is interesting to note that the decomposition of anhydrous $Ni(H_2X)_2$ shows a lesser overlapping of the decarboxylation (the loss of the four COOH groups) and pyrolysis of the incoming residue.

Infrared Spectra. The IR spectra of $[Cu(H_2NTA)_2]\cdot 2H_2O$ and $[Ni(H_2NTA)_2]\cdot 2H_2O$[6,7] are also very similar and show two bands of the ν(C=O) mode of the carboxylic groups at 1740–1735 and 1700 cm^{-1} for the Cu complex and at 1735 and 1672 cm^{-1} for the Ni complex. In addition, the values of $\Delta\nu(COO) = \nu_{as}(COO) - \nu_s(COO)$ for the stretching modes of the carboxylate groups are $1590 - 1370 = 220$ cm^{-1} and $1580 - 1385 = 195$ cm^{-1} for the Cu and Ni chelates, respectively, corresponding to a remarkable ionic character for the carboxylate-to-metal bond in both complexes. The IR spectra (as well as TG-DTA data) of the studied compounds can be rationalized on the basis of a similar structure, the $[Ni(H_2X)_2]\cdot 2H_2O$ complex being less distorted with a lower value of the ν(C=O) band for the carboxylic group to metal ion coordination (1672 cm^{-1}).

Reflectance Spectra. The near-IR–vis–UV spectra of the studied compounds show the characteristic bands of Cu(II) and Ni(II) octahedral complexes. The expected Jahn–Teller effect for the copper compound gives (in part) a dissymmetric broad band at 15 230 cm^{-1} and a shoulder or less intense band at 9800 cm^{-1}, in the spectrum of $[Cu(H_2NTA)_2]\cdot 2H_2O$ (Figure 6, supplementary material). The first band seems to overlap two tetragonal components from $^2B_{1g}$ to $^2B_{2g}$ and ^2E_g, whereas the less intense absorption should correspond to the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition. This latter band is not recorded in the reflectance spectrum of the related compound $[Cu(HNPDA)(H_2O)]$[13] (with a larger distortion of the octahedral environment of the copper atom). In addition, a ligand-to-metal charge-transfer band appears at 36 000 cm^{-1}.

The electronic spectrum of $[Ni(H_2NTA)_2]\cdot 2H_2O$ (Figure 6, supplementary material) shows the following bands: $\nu_1 = 11\,000$ cm^{-1} ($^3T_{2g} \leftarrow {}^3A_{2g}(F)$) and 13 200 cm^{-1} (shoulder, $^1E_g\leftarrow$), $\nu_2 = 17\,400$ cm^{-1} ($^3T_{1g}(F)\leftarrow$), $\nu_3 = 27\,400$ cm^{-1} ($^3T_{1g}(P)\leftarrow$). This octahedral complex should be slightly distorted, and the dissymmetric band around 11 000 cm^{-1} gives only a rough value of $\Delta_0 = 10Dq$. A better value of Δ_0 and of the Racah parameter B can be obtained with the equations proposed by Underhill and Billing:[17]

$$340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0 \qquad (1)$$

$$B = \frac{\nu_2 + \nu_3 - 30Dq}{15} \qquad (2)$$

Solving eq 1, we found Dq values of 1122 and 1250 cm^{-1}, and eq 2 leads us to the corresponding B values of 743 and 487 cm^{-1}. The set of $Dq = 1122$ cm^{-1} and $B = 743$ cm^{-1} values is chosen, as only they lead to a very reasonable prediction of observed bands through the appropriate Tanabe–Sugano diagram (supplementary material) .

Electron Spin Resonance and Magnetic Data. The powder spectra recorded at 298 and 77 K (Figure 7, supplementary material) give to the g values $g_\parallel = 2.25$, $\bar{g} = 2.09$, and $g_\perp = 2.07$ at 298 K ($\bar{g} = 2.08$ at 77 K), consistent with the reported values for an elongated octahedral coordination of copper(II) atoms.[18] The ESR spectra correspond to copper mononuclear complexes in axial symmetry. The parallel band is well-defined. At low temperature, the shape of the spectrum is not affected and its intensity follows Curie's law. Accordingly, for $[Cu(H_2NTA)_2]\cdot 2H_2O$ we found $\mu = 1.74$ μ_B at room temperature and the paramagnetism of this compound also reasonably follows Curie's law (80–300 K; Figure 8, supplementary material). No hyperfine structure can be seen, indicating the presence of interactions between the Cu^{2+} ions (the shortest distance Cu(II)–Cu(II) in the crystal is 6.845 Å). It has been a generally accepted rule for the copper(II) complexes that the visible absorptions shift to shorter wavelengths and the g values become smaller as the copper–ligand bondings in the molecular plane become more covalent.[19] The mean g_0 of the $g_\parallel$ and $g_\perp$ values was plotted against the energies ΔE_{max} at the visible absorption peak and compared with other values of different complexes[19] (Figure 9, supplementary material). It is clear that $[Cu(H_2NTA)_2]\cdot 2H_2O$ is less covalent than the other reported complexes. The correlation between g values and crystal parameters can be established if we consider the coordination about the copper

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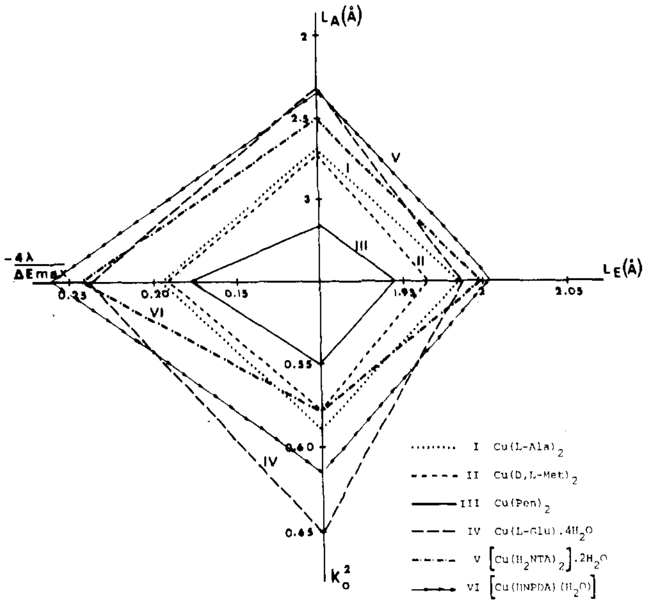

Figure 3. Plot of L_E, L_A, k_0^2, and $-4\lambda/\Delta E_{max}$ of $[Cu(H_2NTA)_2]\cdot 2H_2O$ and related copper(II) complexes: (I) Cu(L-Ala)$_2$; (II) Cu(D,L)-Met)$_2$; (III) Cu(Pen)$_2$; (IV) Cu(L-Glu)$\cdot 2H_2O$; (V) $[Cu(H_2NTA)_2]\cdot 2H_2O$; (VI) $[Cu(HNPDA)(H_2O)]$.

atom. Yokoi et al.[19] have suggested that $k_0^2 = -\Delta E_{max}/4\lambda(g_0 - 2)$ with $\lambda = -825$ cm^{-1} and ΔE_{max} = mean of the two absorption band energies.

The k_0^2 values can be regarded as a measure of the degree of covalency for the copper–ligand bonding. It is of some interest to see how k_0^2 and ΔE_{max} values (supplementary material) correlate with the actual geometry. The plot of L_E ($L_E = {}^1/_2(L_O + L_N)$), L_A, k_0^2, and $-4\lambda/\Delta E_{max}$ (Figure 3) reveals that the complex exhibits some partial ionic character. In fact, if the complex has a smaller circle in Figure 3, the complex becomes more covalent in the coordinate bond. For comparison, we have reported on the same graph the different values of L_E, L_A, k^{02}, and $-4\lambda/\Delta E_{max}$ for the compound $[Cu(HNPDA)(H_2O)]$ and other compounds studied by Yokoi et al. It seems that the complex $[Cu(H_2NTA)_2]\cdot 2H_2O$ is less covalent than $[Cu(HNPDA)(H_2O)]$ and the other complex referred hitherto.

Conclusion

In accordance with the results of Rajabalee, this paper establishes the preparation of $[M(H_2NTA)_2]\cdot 2H_2O$, for M = Cu, Ni. However, the reported crystal structure of $[Cu(H_2NTA)_2]\cdot 2H_2O$ shows that the H_2X^- ion of nitrilotriacetic acid acts doubly as a tridentate chelating agent. This centrosymmetric complex exhibits a shorter Cu–O carboxylic-group-to-copper bond (2.321 Å) than other related complexes with known crystal structures. The bluish violet nickel powder has an unknown crystal structure, but its potentiometric and conductometric titration curves, TG and DTA data, and IR and reflectance spectra strongly suggest the formula $[Ni(H_2NTA)_2]\cdot 2H_2O$, with an octahedral structure similar to and probably less distorted than that of the analogous copper complex. Both solids are so insoluble as to cause copper(II) and nickel(II) precipitation from acid industrial waste waters if they contain a considerable amount of nitrilotriacetic acid. This fact is noticeable, especially if we bear in mind the subsequent remobilization of both metals when the conditions turn to less acid or even alkaline ranges.

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Registry No. $[Cu(H_2NTA)_2]\cdot 2H_2O$, 112621-47-3; $[Ni(H_2NTA)_2]\cdot 2H_2O$, 112621-48-4.

Supplementary Material Available: Tables of thermal motion factors, atomic coordinates and isotropic thermal parameters of hydrogen atoms, C–H and O–H bond lengths (Å), least-squares mean plane equations, torsion and dihedral angles, and van der Waals distances less than 3.70 Å, Figures 4–6, showing potentiometric and conductometric titration curves, TG and DTA diagrams, and reflectance spectra, respectively, a table of observed and calculated bands in the electronic spectrum of $[Ni(H_2NTA)_2]\cdot 2H_2O$, Figures 7–9, showing the ESR spectrum of $[Cu(H_2NTA)_2]\cdot 2H_2O$, a plot of inverse molar susceptibilities of $[Cu(H_2NTA)_2]\cdot 2H_2O$ vs temperature, and a plot of g_0 against ΔE_{max}, respectively, and a table of values of g_0^{-2}, ΔE_{max}, k_0^2, L_A, and L_E in a polycrystalline state (15 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.