$H_2)_3]H[(C_6H_5As)(MoO_4)_3]$, $[C(NH_2)_3]_2[(p\text{-}NH_2C_6H_4As)(MoO_4)_3]\cdot H_2O$, and $[C(NH_2)_3]_2[(p\text{-}HOC_6H_4As)(MoO_4)_3]\cdot 2H_2O$. The latter two salts almost certainly contain 2:6 anions of the type reported here. The first salt however is probably not an acid salt as written but, we believe, contains a tetrameric (4:12) anion analogous to the molybdoarsenate complex $[(HOAs)_4Mo_{12}O_{46}]^{4-}$. We have prepared several such derivatives and reported them elsewhere.[8b,23]

Acknowledgment. The support of this research by the Office of Naval Research is gratefully acknowledged.

Registry No. $[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}]\cdot 6H_2O$, 60364-06-9; $[C(NH_2)_3]_4[(C_6H_5As)_2Mo_6O_{24}]$, 60364-04-7; $[(CH_3)_4N]_4[(C_6H_5As)_2Mo_6O_{24}]$, 60326-17-2; $[C(NH_2)_3]_4[(C_6H_4NH_2As)_2Mo_6O_{24}]$, 60364-03-6; $[(CH_3)_4N]_4[(C_6H_4NH_2As)_2Mo_6O_{24}]$, 60364-02-5; sodium molybdate, 7631-95-0; sodium methylarsonate, 144-21-8; phenylarsonic acid, 98-05-5; *p*-aminophenylarsonic acid, 98-50-0; molybdenum trioxide, 1313-27-5.

Supplementary Material Available: Listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. Rosenheim and R. Bilecki, *Ber. Dtsch. Chem. Ges.*, **46**, 539 (1913).
(2) A. Miolati and R. Pizzighelli, *J. Prakt. Chem.*, **185**, 417 (1908).
(3) P. Souchay, *Bull. Soc. Chim. Fr.*, **15**, 143 (1948).
(4) M. Filowitz and W. G. Klemperer, *J. Chem. Soc., Chem. Commun.*, 233 (1976).
(5) Organoarsonic acids and salts were obtained from ICN Life Sciences Group (K&K), Plainview, N.Y.
(6) In contrast to the main product, this material was optically isotropic, did not give a single-crystal diffraction pattern, and showed additional features in the ir spectrum. Its formation could be minimized by rapid recrystallization.
(7) W. Kwak, M. T. Pope, and T. F. Scully, *J. Am. Chem. Soc.*, **97**, 5735 (1975).
(8) (a) J. K. Stalick and C. O. Quicksall, *Inorg. Chem.*, **15**, 1577 (1976); (b) M. T. Pope, C. O. Quicksall, W. Kwak, L. M. Rajkovic, J. K. Stalick, K. M. Barkigia, and T. F. Scully, paper presented at the 2d International Conference on the Chemistry and Uses of Molybdenum, Oxford, 1976.
(9) Programs used for the structure solution and refinement included local modifications of the ALFF Fourier program by Hubbard, Quicksall, and Jacobson, the Busing–Levy least-squares ORFFE error function and ORABS absorption programs, and Jacobson's ORTEP program.
(10) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(11) T. J. R. Weakley, *Struct. Bonding (Berlin)*, **18**, 131 (1974).
(12) H. T. Evans, Jr., *J. Am. Chem. Soc.*, **96**, 3275 (1968).
(13) M. R. Smith, R. A. Zingaro, and E. A. Meyers, *J. Organomet. Chem.*, **27**, 341 (1971).
(14) K. M. Barkigia, L. M. Rajković, M. T. Pope, and C. O. Quicksall, *J. Am. Chem. Soc.*, **97**, 4146 (1975).
(15) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).
(16) For this reason, the evidence[2,3] for 2:5 complexes of methylarsonate and molybdate should be reexamined.
(17) K. Y. Matsumoto, M. Kato, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 106 (1976).
(18) A. F. Wells, "Structural Inorganic Chemistry", 4th ed, Clarendon Press, Oxford, p 585.
(19) J. Fischer, L. Ricard, and R. Weiss, *J. Am. Chem. Soc.*, **98**, 3050 (1976).
(20) R. Contant, *Bull. Soc. Chim. Fr.*, 3277 (1973).
(21) T. Nishikawa and Y. Sasaki, *Chem. Lett.*, 1185 (1975).
(22) L. Pettersson, *Acta Chem. Scand., Ser. A*, **29**, 677 (1975).
(23) L. M. Rajković and M. T. Pope, work in preparation.

Contribution from the Department of Chemistry,
The Johns Hopkins University, Baltimore, Maryland 21218

Interligand Hydrogen Bonding in Metal–Purine Complexes. Crystal and Molecular Structure of (*N*-3,4-Benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)(aquo)copper(II)

DAVID J. SZALDA, THOMAS J. KISTENMACHER,* and LUIGI G. MARZILLI*

Received June 2, 1976 AIC604411

This report relates the synthesis and crystal structure of (*N*-3,4-benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)(aquo)copper(II). The complex crystallizes from methanol in the monoclinic system, space group $P2_1/c$, with $a = 18.949$ (9) Å, $b = 8.279$ (2) Å, $c = 13.499$ (6) Å, $\beta = 101.60$ (3)°, $Z = 4$, $V = 2074.5$ Å^3, $d_{\text{measd}} = 1.55$ (1) g cm^{-3}, and $d_{\text{calcd}} = 1.56$ g cm^{-3}. The 11 005 reflections in the $+h$ hemisphere to $2\theta = 55°$ were collected by counter methods on a diffractometer employing Mo K$\bar{\alpha}$ radiation and the θ–2θ scan technique. The 11 005 measured reflections were subsequently reduced to a set of 4174 independent, symmetry-averaged reflections with $I > \sigma(I)$, which were used in the structural solution and refinement. The structure was solved by standard heavy-atom Patterson and Fourier methods and has been refined by full-matrix least squares, based on F, to a final R value of 0.068. The copper(II) is in a pseudo-square-pyramidal environment with the tridentate Schiff base and N(7) of the theophyllinato ligand, Cu–N(7) = 2.000 (3) Å, in the equatorial positions and a weakly bound water molecule, Cu–OH$_2$ = 2.740 (3) Å, in the axial position. There are two interligand hydrogen bonds to the O(6) carbonyl oxygen of the theophyllinato ligand, one from the secondary amine of the ethylenediamine terminus of the Schiff base chelate and one from the axially bonded water molecule. The Cu–N(7) vector lies 15.5 (3)° out of the plane of the theophyllinato ligand, probably as a consequence of the axial interligand hydrogen bond. The crystal packing is dominated by intercomplex hydrogen bonding and the formation of two types of stacking dimers between symmetry-related complexes, one employing the naphthylidene ring of the Schiff base and one the theophylline monoanion ring.

Introduction

An integral part of our work on stereoselective metal–ligand and ligand–ligand interactions in chelate–transition metal complexes of purines, pyrimidines, and their nucleosides has centered on copper(II) complexes of the tridentate ligand *N*-salicylidene-*N*′-methylethylenediamine. The Cu(II) complex of this Schiff base has one equatorial coordination site available for ligand attachment. The exocyclic oxygen atom of the salicylidene ring is a potential hydrogen-bond acceptor site, and the amino group at the *N*-methylethylenediamine terminus is a potential hydrogen-bond donor site.

Thus far we have studied the crystal and molecular structures of three complexes of the above Schiff base system: (1) in the theophyllinato complex,[1] the metal binding is at N(7) of the purine and an interligand hydrogen bond is formed between the coordinated secondary amine group on the Schiff base and the exocyclic carbonyl oxygen, O(6), on the coordinated purine atom; (2) in the 9-methyladenine complex,[2] the metal binding site is N(7) and an interligand hydrogen bond is formed between the coordinated salicylidene oxygen

Table I. Crystal Data for (*N*-3,4-Benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)(aquo)copper(II)

$a = 18.949\ (9)$ Å	$Cu(O_3N_6C_{21}H_{22})\cdot H_2O$
$b = 8.279\ (2)$ Å	Mol wt 488.0
$c = 13.499\ (6)$ Å	$d_{measd} = 1.55\ (1)\ g\ cm^{-3}$
$\beta = 101.60\ (3)°$	$d_{calcd} = 1.56\ g\ cm^{-3}$
$V = 2074.5\ Å^3$	Space group $P2_1/c$
$Z = 4$	$\mu = 11.3\ cm^{-1}$
$\lambda(Mo\ K\bar{\alpha}) = 0.710\ 69$ Å	

and the exocyclic amino group at C(6) of the coordinated purine; (3) in the cytosine complex,[3] the metal binding site is N(3) of the pyrimidine ring and the exocyclic carbonyl oxygen O(2) forms both an interligand hydrogen bond to the secondary amine of the Schiff base and an axial bond to the copper(II) center.

In this report, we describe the synthesis and molecular and crystal structure of the theophylline monoanion complex of the (*N*-3,4-benzosalicylidene-*N*′-methylethylenediamine)copper(1+) cation. This complex cation closely resembles, near the potential equatorial binding site, the salicylidene system employed in the previous studies.[1-3] The interligand interactions we have observed in the present system, however, provide yet a different mode of interligand interaction in such compounds.

Experimental Section

Preparation of (*N*-3,4-Benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)(aquo)copper(II). The complex (chloro)(*N*-3,4-benzosalicylidene-*N*′-methylethylenediamine)copper(II) was prepared by a modification of the method of Sacconi and Bertini.[4,5] A solution of the aquated cation was obtained by adding aqueous $AgNO_3$ (0.16 g, 1 mmol) to a solution of the chloro complex (0.34 g, 1 mmol) in 20 ml of methanol. The precipitated AgCl was removed by filtration, and theophylline (0.18 g, 1 mmol) and KOH (1 mmol) were then added to the filtrate.

The crystals of the desired product which formed after about 1 day were of poor quality. They were subsequently redissolved in methanol, and the solvent was allowed to evaporate slowly. After about 1 week, reddish brown crystals suitable for x-ray measurements were collected. The magnetic moment of the theophyllinato complex, 1.9 μ_B, was measured on a Faraday balance (22 °C) and corrected for diamagnetic effects.[6] The observed magnetic moment is typical of those we have measured for pseudo-square-pyramidal complexes of copper(II) with purine and pyrimidine ligands.[7]

Collection and Reduction of the X-Ray Diffraction Data. The title complex crystallizes as elongated prisms with *c* as the prism axis. Preliminary Weissenberg and oscillation photographs showed the crystal system to be monoclinic with systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) consistent with the space group $P2_1/c$. Unit cell dimensions and their associated standard deviations were derived on the basis of a least-squares fit to the 2θ, ω, and χ setting angles for 15 carefully centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer. The crystal density, measured by neutral buoyancy methods in a mixed-solvent system, indicated one formula unit per asymmetric volume. Complete crystal data are given in Table I.

The 11 005 reflections in the $+h$ hemisphere to $2\theta = 55°$ were measured on the diffractometer, employing Mo $K\bar{\alpha}$ graphite-monochromated radiation. The crystal used in data collection had dimensions 0.25 × 0.25 × 0.10 mm. The intensity measurements were made in the θ–2θ scan mode; individual scan speeds, 2–24° min^{-1}, were determined by a rapid scan at the calculated Bragg peak. Three reflections were monitored after every 100 reflections during the course of the experiment; their intensities showed no systematic trends, the maximum deviation of any standard from its mean intensity being about 5%. The 11 005 measured intensities were reduced to a set of 9960 values by the exclusion of standards and systematic absences. Individual reflections were assigned observational variances based on the equation

$$\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$$

where S, B_1, and B_2 are the scan and background extremum counts, T_S and T_B are the scan and individual background counting times ($T_B = 1/4T_S$ for all measurements), and p was taken to be equal to 0.04 and represents the expected error proportional to the diffracted intensity[8] as determined by the random variations in the integrated counts for the standard reflections. The intensities and their standard deviations were corrected for Lorentz and polarization effects, but no correction for absorption was applied [$\mu = 11.3\ cm^{-1}$]; the maximum error introduced by neglect of absorption effects was estimated to be about 4% in F. The 9960 squared structure factors were subsequently combined to yield 4174 symmetry-independent values with $I > \sigma(I)$. An approximate absolute scale was determined by the method of Wilson.[9]

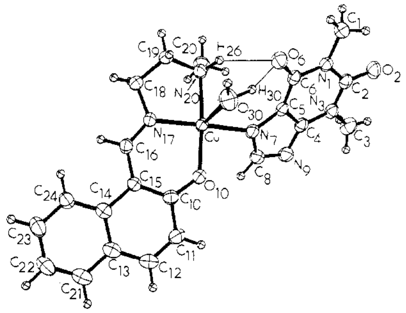


Figure 1. Perspective view of the molecular conformation of the complex (*N*-3,4-benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)copper(II). The thermal ellipsoids are drawn at the 50% probability level; the hydrogen atoms have been assigned arbitrary thermal parameters of 1.0 Å^2 for this and subsequent drawings.

Solution and Refinement of the Structure. The position of the copper was determined from a three-dimensional Patterson synthesis. A structure factor Fourier calculation based on the copper allowed the positioning of the remaining 31 nonhydrogen atoms in the asymmetric unit (R(all atoms included) $= \sum\|F_o| - |F_c\|/\sum|F_o| = 0.22$). Three cycles of full-matrix, isotropic least squares, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, plus one cycle of anisotropic refinement on the nonhydrogen atoms reduced the R value to 0.091. A difference Fourier was then computed and positional parameters for the 24 hydrogens in the asymmetric unit were derived. The hydrogen atoms were assigned temperature factors based on the heavy atoms to which they were bonded. No attempt has been made to refine any of the hydrogen atom parameters. Two further cycles of anisotropic refinement led to convergence (all shift per error values less than 1) and to a final R value of 0.068. The final weighted R value [$R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$] and goodness of fit [$(\sum w(|F_o| - |F_c|)^2/(NO - NV))^{1/2}$, where NO = 4174 observations and NV = 289 variables] were 0.055 and 1.9, respectively.

Neutral scattering factor curves for all nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman,[10] while the scattering curve for hydrogen was that of Stewart, Davidson, and Simpson.[11] The real part of the scattering curve for Cu was corrected for anomalous dispersion effects.[12] Final nonhydrogen parameters are collected in Table II. Hydrogen atom parameters are given in Table III. A complete list of calculated and observed structure factor amplitudes is available.[13]

The crystallographic computations were performed with the following programs: structure factor Fourier, X-RAY 67;[14] least squares, a modified version of ORFLS;[15] best planes, MEAN PLANE;[16] illustrations, ORTEP.[17] Calculations not cited were performed with locally written programs.

Results and Discussion

The molecular conformation of the title complex is illustrated in Figure 1. The primary coordination sphere about the copper(II) is pseudo square pyramidal with the tridentate Schiff base chelate and N(7) of the theophyllinato ligand, Cu–N(7) = 2.000 (3) Å, occupying the four equatorial positions and a water molecule, Cu–O(30)H_2 = 2.740 (3) Å, in one of the axial positions. The Cu–O(30)H_2 distance is significantly longer than we have observed in similar systems.[2,18-20] As we have noted before, however, the coordinated water is trans to the axial methyl group of the ethylenediamine system.[2]

Table II. Final Nonhydrogen Atom Parameters ($\times 10^4$)[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	7 237 (0.2)	1596 (0.5)	1493 (0.3)	18 (0.1)	143 (0.6)	35 (0.2)	9 (0.2)	7 (0.1)	16 (0.4)
O(2)	10 593 (1)	−1237 (3)	4327 (2)	25 (1)	199 (5)	54 (2)	20 (2)	4 (1)	14 (2)
O(6)	9 103 (1)	2736 (3)	2794 (2)	30 (1)	110 (4)	62 (2)	2 (1)	3 (1)	14 (2)
O(10)	6 449 (1)	903 (3)	2065 (2)	21 (1)	216 (5)	46 (1)	11 (2)	8 (1)	36 (2)
O(30)	7 730 (1)	4295 (3)	2591 (2)	35 (1)	173 (5)	68 (2)	5 (2)	2 (1)	−17 (3)
N(1)	9 849 (1)	687 (3)	3485 (2)	22 (1)	130 (5)	37 (2)	4 (2)	7 (1)	5 (2)
N(3)	9 435 (1)	−1956 (3)	3699 (2)	25 (1)	117 (5)	45 (2)	16 (2)	9 (1)	16 (2)
N(7)	7 881 (1)	205 (3)	2501 (2)	21 (1)	119 (5)	40 (2)	6 (2)	7 (1)	12 (2)
N(9)	8 152 (1)	−2346 (4)	3085 (2)	26 (1)	128 (5)	62 (2)	6 (2)	11 (1)	22 (3)
N(17)	6 592 (1)	2530 (3)	341 (2)	19 (1)	144 (5)	37 (2)	6 (2)	5 (1)	16 (2)
N(20)	8 020 (1)	2262 (3)	762 (2)	20 (1)	147 (5)	34 (1)	3 (2)	4 (1)	−1 (2)
C(1)	10 467 (2)	1757 (5)	3638 (3)	28 (1)	189 (7)	50 (2)	−17 (3)	4 (1)	2 (3)
C(2)	9 996 (2)	−872 (4)	3867 (2)	23 (1)	146 (6)	34 (2)	15 (2)	10 (1)	3 (3)
C(3)	9 573 (2)	−3627 (4)	3991 (3)	37 (1)	136 (7)	72 (3)	24 (2)	14 (2)	33 (3)
C(4)	8 755 (2)	−1451 (4)	3240 (2)	23 (1)	123 (5)	36 (2)	10 (2)	10 (1)	6 (3)
C(5)	8 620 (2)	110 (4)	2898 (2)	22 (1)	111 (5)	32 (2)	9 (2)	8 (1)	6 (2)
C(6)	9 166 (2)	1300 (4)	3030 (2)	24 (1)	117 (6)	30 (2)	7 (2)	7 (1)	3 (2)
C(8)	7 651 (2)	−1282 (4)	2638 (3)	23 (1)	136 (6)	54 (2)	3 (2)	9 (1)	11 (3)
C(10)	5 764 (2)	1067 (4)	1711 (2)	23 (1)	134 (6)	44 (2)	2 (2)	11 (1)	−1 (3)
C(11)	5 294 (2)	269 (5)	2263 (3)	31 (1)	165 (7)	49 (2)	2 (2)	14 (1)	16 (3)
C(12)	4 569 (2)	386 (4)	1982 (3)	26 (1)	150 (7)	66 (3)	−10 (2)	18 (1)	−4 (3)
C(13)	4 236 (2)	1311 (4)	1132 (3)	22 (1)	107 (6)	64 (2)	−6 (2)	12 (1)	−19 (3)
C(14)	4 676 (2)	2093 (4)	536 (2)	21 (1)	97 (5)	53 (2)	2 (2)	8 (1)	−16 (3)
C(15)	5 455 (2)	1924 (4)	821 (2)	19 (1)	110 (5)	44 (2)	2 (2)	7 (1)	−2 (3)
C(16)	5 898 (2)	2553 (4)	178 (2)	22 (1)	125 (6)	36 (2)	6 (2)	4 (1)	2 (3)
C(18)	6 958 (2)	3131 (5)	−450 (2)	22 (1)	202 (8)	42 (2)	6 (2)	8 (1)	27 (3)
C(19)	7 714 (2)	3593 (4)	68 (2)	22 (1)	180 (7)	46 (2)	3 (2)	10 (1)	26 (3)
C(20)	8 286 (2)	911 (5)	228 (3)	24 (1)	172 (7)	51 (2)	−1 (2)	11 (1)	−17 (3)
C(21)	3 478 (2)	1486 (5)	862 (3)	24 (1)	156 (7)	86 (3)	−9 (2)	16 (1)	−12 (4)
C(22)	3 163 (2)	2376 (5)	55 (4)	19 (1)	172 (7)	104 (4)	−2 (2)	3 (2)	−2 (4)
C(23)	3 592 (2)	3156 (5)	−532 (3)	24 (1)	175 (8)	84 (3)	11 (2)	1 (2)	8 (4)
C(24)	4 328 (2)	3022 (4)	−290 (3)	22 (1)	151 (7)	60 (2)	3 (2)	4 (1)	4 (3)

[a] Estimated standard deviations in the least significant figures in this and the following tables are enclosed in parentheses. The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table III. Hydrogen Atom Positional ($\times 10^3$) and Isotropic Thermal Parameters

Atom	x	y	z	B,[a] Å^2
H(1)[C(1)]	1071	191	429	4.5
H(2)[C(1)]	1089	147	323	4.5
H(3)[C(1)]	1036	285	348	4.5
H(4)[C(3)]	964	−426	348	4.8
H(5)[C(3)]	919	−412	420	4.8
H(6)[C(3)]	993	−382	438	4.8
H(8)[C(8)]	715	−158	243	4.0
H(11)[C(11)]	551	−34	286	4.5
H(12)[C(12)]	426	−17	234	4.5
H(16)[C(16)]	565	301	−45	4.5
H(17)[C(18)]	670	403	−81	4.3
H(18)[C(18)]	697	229	−95	4.3
H(19)[C(19)]	770	458	46	4.3
H(20)[C(19)]	802	379	−40	4.3
H(21)[C(21)]	318	94	126	4.5
H(22)[C(22)]	265	248	−9	5.2
H(23)[C(23)]	335	375	−113	5.2
H(24)[C(24)]	462	360	−69	4.5
H(26)[N(20)]	840	260	120	4.0
H(27)[C(20)]	854	6	71	4.5
H(28)[C(20)]	791	15	−16	4.5
H(29)[C(20)]	869	109	−14	4.5
H(30)[O(30)]	821	371	284	6.2
H(31)[O(30)]	786	547	268	6.2

[a] The hydrogen atom isotropic thermal parameters were set about equal to the isotropic thermal parameters of the atom to which they are attached [enclosed in brackets].

The presence of the coordinated secondary amine, N(20), and the axial water molecule in the primary coordination sphere offers to the theophyllinato ligand two possible donors for formation of an interligand hydrogen bond to O(6) of the purine ring system. In this case, *both* potential interligand hydrogen-bonding schemes are present, with a strong hydrogen bond between the axial water and O(6) [O(30)···O(6) = 2.868 (4) Å, H(30)···O(6) = 1.88 Å, O(30)–H(30)···O(6) = 159°] and a moderate intramolecular hydrogen bond between N(20) and O(6) [N(20)···O(6) = 3.103 (4) Å, H(26)···O(6) = 2.29 Å, N(20)–H(26)···O(6) = 152°]. In contrast, the closely related complex (*N*-salicylidene-*N'*-methylethylenediamine)(theophyllinato)copper(II)) is approximately square planar with a strong intramolecular hydrogen bond between N(20) and O(6).[1]

In order to accommodate both interligand hydrogen bonds, the dihedral angle between the purine and the equatorial plane increases from 33.8 (1)° in the salicylidene complex[1] to 44.7 (1)° in the benzosalicylidene system; the opening of this dihedral angle is consistent with the formation of a weaker hydrogen bond to the equatorial amine N(20) as compared to that to the salicylidene complex. Furthermore, N(7) in the present system is significantly pyramidal with the sum of the angles at N(7) being equal to 356.2 (3)° [the analogous sum in the salicylidene complex is 359.9 (1)°]. The pyramidal hybridization at N(7) is most clearly identifiable with a movement of the Cu atom out of the plane of the theophylline anion by 0.536 Å leading to an angle of 15.5 (3)° between the Cu–N(7) vector and the plane of the theophyllinato ligand. The analogous angle in the salicylidene complex is only 2.5 (1)°. However, it is not uncommon for other metal–purine complexes containing an axial hydrogen bond to display a significant angle between the Cu–N(7) vector and the plane of the purine. For example, in the complex cation triaquobis(9-methylguanine)copper(2+) there are interligand hydrogen bonds from an axial water molecule, Cu–O = 2.704 (5) Å, to O(6) of the two coordinated 9-methylguanine ligands.[21] In both purine ligands the coordinated N(7) atoms are pyramidal [sums of the angles 357.2 (4) and 358.1 (4)°, respectively] and the angles between the Cu–N(7) bonds and the purine planes are 15.6 (5) and 15.9 (5)°.[21] Furthermore,

Table IV. Nonhydrogen Atom Interatomic Distances (Å) and Angles (deg)

(a) Primary Coordination Sphere about the Copper Atom

Bond Lengths

Cu-N(7)	2.000 (3)	Cu-O(10)	1.902 (2)
Cu-N(17)	1.936 (3)	Cu-O(30)	2.740 (3)
Cu-N(20)	2.018 (3)		

Bond Angles

N(7)-Cu-N(17)	167.7 (1)	N(17)-Cu-N(20)	84.5 (1)
N(7)-Cu-N(20)	94.7 (1)	N(17)-Cu-O(10)	91.5 (1)
N(7)-Cu-O(10)	88.4 (1)	N(20)-Cu-O(10)	174.7 (1)
N(7)-Cu-O(30)	90.4 (1)	N(20)-Cu-O(30)	80.6 (1)
N(17)-Cu-O(30)	101.6 (1)	O(10)-Cu-O(30)	103.7 (1)

(b) *N*-3,4-Benzosalicylidene-*N'*-methylethylenediamine Chelate Ligand

Bond Lengths

O(10)-C(10)	1.298 (4)	C(15)-C(16)	1.423 (4)
C(10)-C(11)	1.431 (5)	C(16)-N(17)	1.290 (4)
C(11)-C(12)	1.355 (5)	N(17)-C(18)	1.471 (4)
C(12)-C(13)	1.417 (5)	C(18)-C(19)	1.511 (5)
C(13)-C(14)	1.425 (5)	C(19)-N(20)	1.486 (4)
C(13)-C(21)	1.416 (5)	N(20)-C(20)	1.472 (4)
C(14)-C(24)	1.406 (5)	C(21)-C(22)	1.350 (6)
C(14)-C(15)	1.455 (4)	C(22)-C(23)	1.403 (6)
C(15)-C(10)	1.416 (4)	C(23)-C(24)	1.371 (5)

Bond Angles

Cu-O(10)-C(10)	128.9 (2)	C(14)-C(15)-C(16)	119.7 (3)
O(10)-C(10)-C(11)	116.1 (3)	C(15)-C(16)-N(17)	126.7 (3)
O(10)-C(10)-C(15)	125.2 (3)	C(16)-N(17)-C(18)	119.0 (3)
C(11)-C(10)-C(15)	118.6 (3)	Cu-N(17)-C(16)	126.9 (2)
C(10)-C(11)-C(12)	121.5 (3)	Cu-N(17)-C(18)	113.9 (2)
C(11)-C(12)-C(13)	121.8 (3)	N(17)-C(18)-C(19)	106.9 (3)
C(12)-C(13)-C(14)	119.2 (3)	C(18)-C(19)-N(20)	108.5 (3)
C(12)-C(13)-C(21)	121.8 (3)	Cu-N(20)-C(19)	106.2 (2)
C(14)-C(13)-C(21)	119.1 (3)	Cu-N(20)-C(20)	112.9 (2)
C(13)-C(14)-C(15)	119.0 (3)	C(19)-N(20)-C(20)	112.6 (3)
C(13)-C(14)-C(24)	117.6 (3)	C(13)-C(21)-C(22)	121.7 (4)
C(15)-C(14)-C(24)	123.5 (3)	C(21)-C(22)-C(23)	119.6 (4)
C(10)-C(15)-C(14)	119.8 (3)	C(22)-C(23)-C(24)	120.4 (4)
C(10)-C(15)-C(16)	120.5 (3)	C(14)-C(24)-C(23)	121.7 (3)

(c) Theophylline Anion

Bond Lengths

N(1)-C(1)	1.450 (4)	N(7)-C(5)	1.398 (4)
N(1)-C(2)	1.396 (4)	N(7)-C(8)	1.331 (4)
N(1)-C(6)	1.411 (4)	N(9)-C(4)	1.343 (4)
N(3)-C(2)	1.375 (4)	N(9)-C(8)	1.346 (4)
N(3)-C(3)	1.448 (5)	C(2)-O(2)	1.212 (4)
N(3)-C(4)	1.377 (4)	C(4)-C(5)	1.378 (4)
C(5)-C(6)	1.413 (4)	C(6)-O(6)	1.230 (4)

Bond Angles

C(1)-N(1)-C(2)	114.7 (3)	N(1)-C(2)-N(3)	116.9 (3)
C(1)-N(1)-C(6)	119.1 (3)	N(3)-C(4)-N(9)	126.3 (3)
C(2)-N(1)-C(6)	126.2 (3)	N(3)-C(4)-C(5)	121.9 (3)
C(2)-N(3)-C(3)	119.2 (3)	N(9)-C(4)-C(5)	111.8 (3)
C(2)-N(3)-C(4)	119.9 (3)	N(7)-C(5)-C(4)	106.6 (3)
C(3)-N(3)-C(4)	121.0 (3)	N(7)-C(5)-C(6)	131.3 (3)
Cu-N(7)-C(5)	136.1 (2)	C(4)-C(5)-C(6)	122.0 (3)
Cu-N(7)-C(8)	117.0 (2)	N(1)-C(6)-O(6)	119.5 (3)
C(5)-N(7)-C(8)	103.1 (3)	N(1)-C(6)-C(5)	112.8 (3)
C(4)-N(9)-C(8)	102.1 (3)	C(5)-C(6)-O(6)	127.7 (3)
N(1)-C(2)-O(2)	121.0 (3)	N(7)-C(8)-N(9)	116.5 (3)
N(3)-C(2)-O(2)	122.2 (3)		

Table V. Least-Squares Planes and Deviations of Individual Atoms from These Planes[a]

(a) Primary Coordination Plane Including the Copper Atom ($-0.0071X - 0.8304Y - 0.5571Z = -2.1808$ Å)

Cu	−0.111	N(7)	0.096
O(10)	−0.044	N(17)	0.102
O(30)	−2.780*	N(20)	−0.042

(b) 3,4-Benzosalicylidene Ring ($0.0791X - 0.8124Y - 0.5778Z = -1.1523$ Å)

C(10)	−0.045	C(15)	0.031
C(11)	−0.013	C(21)	−0.003
C(12)	0.021	C(22)	−0.015
C(13)	0.016	C(23)	−0.014
C(14)	0.025	C(24)	−0.004

(c) Nine-Atom Framework of the Coordinated Theophylline Anion ($0.3697X - 0.2607Y - 0.8918Z = 2.2795$ Å)

N(1)	0.013	C(5)	0.028
C(2)	−0.036	C(6)	−0.016
N(3)	0.020	N(7)	−0.003
C(4)	0.022	C(8)	−0.018
O(2)	−0.128*	N(9)	−0.009
O(6)	−0.068*	C(1)	0.019*
Cu	0.536*	C(3)	0.103*

(d) Imidazole Ring of the Coordinated Theophylline Anion ($0.3499X - 0.2694Y - 0.8972Z = 1.9766$ Å)

N(7)	−0.002	C(4)	0.000
N(9)	−0.001	C(5)	0.001
		C(8)	0.002

(e) Pyrimidine Ring of the Coordinated Theophylline Anion ($0.3838X - 0.2553Y - 0.8874Z = 2.5379$ Å)

N(1)	0.028	C(4)	−0.003
N(3)	0.012	C(5)	0.006
C(2)	−0.024	C(6)	−0.018

[a] In each of the equations of the planes, X, Y, and Z are coordinates (Å) referred to the orthogonal axes a, b, and c^*. Atoms indicated by an asterisk were given zero weight in calculating the planes; other atoms were equally weighted.

when 9-methyladenine is coordinated through N(7) and involved in an interligand hydrogen bond to an axial water [$N(6)H_2 \cdots OH_2$], as in the 9-methyladenine complex of glycylglycinatocopper(II),[20] the sum of the angles at N(7) is 358.8 (1)° and the displacement of the Cu–N(7) vector from the adenine plane is 9.2 (1)°. However, when the interligand hydrogen bond is formed to an equatorial site, as in the salicylidene complex of the theophyllinato ligand[1] and the 9-methyladenine complex of the same system [where a $N(6)H_2 \cdots O(10)$ hydrogen bond is formed][2], N(7) is essentially trigonal planar and the deviation of the Cu–N(7) bond from the purine plane is nominal (2.5 (1)° for the theophyllinato system[1] and 1.6 (3)° for the 9-methyladenine system[2]).

It may be expected in copper(II) complexes, then, that when coordinated purines partake in interligand hydrogen bonding with axial sites in the coordination sphere, there will be a significant pyramidal hybridization at N(7) and a displacement of the Cu–N(7) vector from the mean plane of the purine of 10–15°. Both of these effects are, however, severely muted when interligand hydrogen bonding involves an equatorial site in the coordination sphere.

Intramolecular Bond Lengths and Bond Angles. A complete list of intramolecular bond lengths and angles is contained in Table IV. The Cu–N(7) bond length, 2.000 (3) Å, is significantly longer than observed in the salicylidene complex, 1.986 (1) Å, and this increase is probably related to two features: (1) the increase in coordination geometry from 4 in the salicylidene complex to 4 + 1 in the benzosalicylidene complex; (2) the displacement of the Cu out of the plane of the purine plane and the consequent pyramidal hybridization at N(7) in the benzosalicylidene complex. The rest of the geometry in the primary coordination sphere is fairly similar in the two complexes, although there is an increase in the N(20)–Cu–O(10) bond angle from 171.9 (1)° in the salicylidene complex[1] to 174.7 (1)° in the benzosalicylidene complex, and this increase is probably related to the greater planarity in the primary coordination sphere of the benzosalicylidene system, Table V.

The parameters in the coordinated theophyllinato ligand, Table IV, are in good agreement with other complexes we have studied,[1,22,23] with the exception of slight variations in the exocyclic bond lengths and bond angles which are more susceptible to their immediate environment. The exocyclic

Table VI. Distances and Angles in Interactions of the Type D–H· · ·A

D	H	A	D–H, Å	D· · ·A, Å	H· · ·A, Å	D–H· · ·A, deg
			Hydrogen Bonds			
N(20)	H(26)	O(2)[a]	0.89	2.931	2.36	122.3
N(20)	H(26)	O(6)[b]	0.89	3.103	2.29	151.8[d]
O(30)	H(30)	O(6)[b]	1.03	2.868	1.88	159.2[d]
O(30)	H(31)	N(9)[c]	1.00	2.933	1.94	170.5
			Other Interactions			
C(8)	H(8)	O(10)[b]	0.97	2.890	2.44	107.9

[a] $2-x, {}^1/_2+y, {}^1/_2-z$. [b] x, y, z. [c] $x, 1+y, z$. [d] Interligand hydrogen bond.

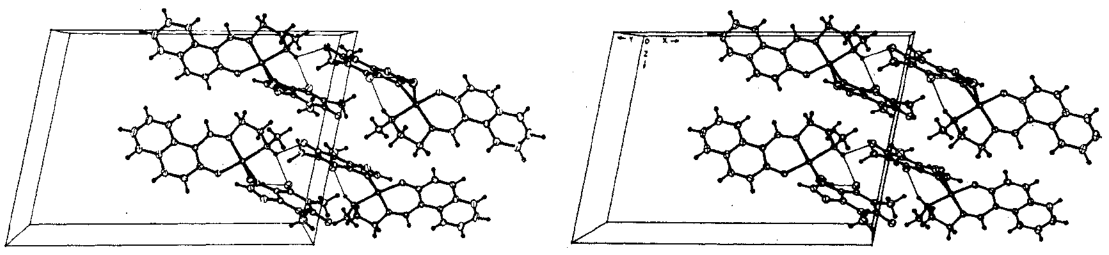


Figure 2. Stereoview of the unit cell packing. The *a* axis is horizontal, the *c* axis vertical, and the *b* axis is toward the viewer.

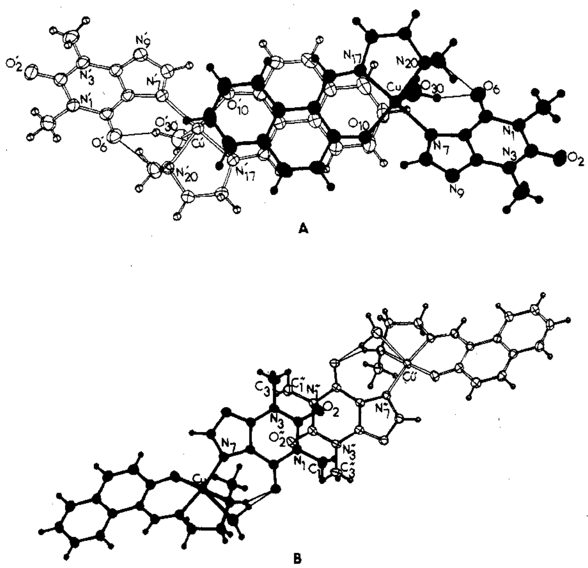


Figure 3. (A) Stacking of the benzosalicylidene rings about the inversion center at $^1/_2$, 0, 0. (B) Stacking of the theophyllinato rings about the inversion center at 1, 0, $^1/_2$.

bond angles at N(7), Cu–N(7)–C(5) and Cu–N(7)–C(8), are 136.1 (2) and 117.0 (2)°, respectively. These values are consistent with those of other N(7)-bonded Cu(II) purines exhibiting intramolecular hydrogen bonding.[7] The purine anion is reasonably planar, Table V, with a dihedral angle between the imidazole and pyramidine rings of 2.2 (1)° which is a common feature of coordinated purine anions.[1,22,23]

We know of only one other benzosalicylidene Schiff base for which crystallographic data are available, bis(*N*-methyl-3,4-benzosalicylideniminato)copper(II).[24] Our parameters are in good agreement with the values in that complex, although the poorer accuracy in that structure precludes any detailed comparison. The naphthylidene ring system is reasonably planar, Table V, with a fold about the C(13)–C(14) bond of 2.0 (1)°.

Crystal Packing. The crystal packing is illustrated in the stereoview of Figure 2. Three principal features dominate the observed packing. (1) Intercomplex hydrogen bonding is present between symmetry-related complexes. The secondary amine of the Schiff base, besides partaking in the intracomplex hydrogen bonding to O(6), forms a weak hydrogen bond to the O(2) carbonyl oxygen of a screw-related complex, and the coordinated water molecule employs its second hydrogen atom to form a strong intercomplex hydrogen bond to N(9) of a translationally related complex. Details of these intercomplex hydrogen bonds are given in Table VI. (2) Inversion-related complexes [about $^1/_2$, 0, 0] show significant overlap, Figure 3A, involving the terminal benzo ring of the benzosalicylidene system and the six-membered chelate ring about the copper. There are no close contacts in this stacking; however, C(22) of one complex comes within 3.888 (3) Å of the copper atom of the inversion-related complex and approximately occupies the open axial position about the copper, Figure 3A. (3) Inversion-related complexes [about 1, 0, $^1/_2$] show significant dipolar overlap of the pyrimidine rings of the theophylline monoanion, Figure 3b. The mean stacking distance in the theophylline monoanion dimers is 3.31 Å, and there are several contacts worthy of mention: O(2)···N(1″), 3.260 (5) Å; O(2)···C(2″), 3.366 (5) Å; C(2)···C(2″), 3.380 (5) Å. The strength of the stacking of the theophylline monoanions is evidenced by the close approach of the carbon atoms of the exocyclic methyl substituents, $C(3)H_3 \cdots C(1'')H_3$, 3.570 (5) Å.

Acknowledgment. This investigation was supported by the National Institutes of Health, Public Health Service Grant No. GM 20544.

Registry No. (*N*-3,4-Benzosalicylidene-*N*′-methylethylenediamine)(theophyllinato)(aquo)copper(II), 60306-14-1; (chloro)(*N*-3,4-benzosalicylidene-*N*′-methylethylenediamine)copper(II), 60306-15-2.

Supplementary Material Available: Listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

References and Notes

(1) T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Inorg. Chem.*, **14**, 1686 (1975).
(2) D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, *Inorg. Chem.*, **14**, 2623 (1975).
(3) D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, **14**, 2076 (1975).
(4) We thank Miss Gwenn Pavlovitz for the synthesis of the benzosalicylidene Schiff base.
(5) L. Sacconi and I. Bertini, *Inorg. Chem.*, **5**, 1520 (1966).
(6) W. L. Jolly, "Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970.
(7) T. J. Kistenmacher and L. G. Marzilli, paper presented at the 9th Jerusalem Symposium, April 1975; also work to be submitted for publication.

(8) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(9) A. J. C. Wilson, *Nature* (London), **150**, 152 (1942).
(10) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(13) Supplementary material.
(14) J. M. Stewart, "X-RAY 67", Technical Report 67-58, Computer Science Center, University of Maryland, 1967.
(15) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(16) M. E. Pippy and F. R. Ahmed, "NRC Crystallographic Programs", National Research Council, Ottawa, 1968.
(17) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(18) T. J. Kistenmacher and D. J. Szalda, *Acta Crystallogr., Sect. B*, **31**, 1659 (1975).
(19) T. J. Kistenmacher, T. Sorrell, and L. G. Marzilli, *Inorg. Chem.*, **14**, 2479 (1975).
(20) T. J. Kistenmacher, L. G. Marzilli, and D. J. Szalda, *Acta Crystallogr., Sect. B*, **32**, 186 (1976).
(21) E. Sletten and N. Flogstad, *Acta Crystallogr., Sect. B*, **32**, 461 (1976).
(22) T. Sorrell, L. G. Marzilli, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **98**, 2181 (1976).
(23) D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, to be submitted for publication.
(24) D. W. Martin and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 2440 (1973).

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Structural Studies of Triazenido Complexes. 1. Crystal and Molecular Structure of *trans*-Bis(triphenylphosphine)carbonyl(1,3-di-*p*-tolyltriazenido)hydridoruthenium(II), *trans*-[Ru(H)($CH_3C_6H_4N_3C_6H_4CH_3$)(CO)($P(C_6H_5)_3)_2$]

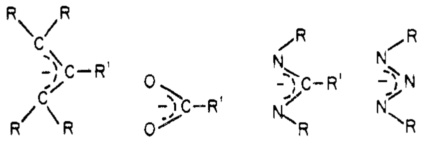
LEO D. BROWN and JAMES A. IBERS*

Received May 19, 1976 AIC60366U

The structure of *trans*-bis(triphenylphosphine)carbonyl(1,3-di-*p*-tolyltriazenido)hydridoruthenium(II) has been determined from three-dimensional x-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two molecules in the unit cell of dimensions a = 14.074 (2) Å, b = 15.264 (3) Å, c = 12.195 (2) Å, α = 109.78 (1)°, β = 111.74 (1)°, γ = 65.03 (1)°, and V = 2154 Å^3; ρ_{calcd} = 1.35 and ρ_{obsd} = 1.34 g cm^{-3}. A full-matrix least-squares refinement of the structure by standard procedures resulted in an R index of 0.038 for the 5847 independent data for which $F_o^2 > 3\sigma(F_o^2)$. The coordination about the ruthenium atom is approximately octahedral. The triazenido ligand is coordinated to the metal atom in a bidentate mode with a N(1)–Ru–N(3) angle of 57.7 (1)° and a N(1)–N(2)–N(3) angle of 105.2 (3)°. The Ru–N(3) bond length is 2.179 (3) Å compared with the Ru–N(1) distance of 2.149 (3) Å. The N–N bond lengths within the triazenido moiety are equal with N(1)–N(2) and N(2)–N(3) distances of 1.318 (4) and 1.310 (4) Å, respectively. The entire ruthenium–triazenido system is essentially planar, indicative of π delocalization over the whole system.

Introduction

The study of transition metal complexes containing triazenido ligands has increased greatly in the last few years. Although isoelectronic with allyl (I), carboxylato (II), and



I II III IV

amidino (III), the triazenido ligand (IV) had not received much interest compared with the former ligands. Owing to the fact that each of these anions is potentially either a two- or four-electron donor, much research has centered on the preferred bonding arrangement of the ligand in a given system.

As early as 1941, Dwyer and Mellor[1] proposed that 1,3-diphenyltriazenido (dpt) complexes of nickel contained bidentate triazenido ligands, resulting in a strained four-membered chelate ring. This formulation was later disputed[2] and ultimately shown to be incorrect. Structural studies of $[Ni(dpt)_2]_2$,[3,4] $[Cu(dpt)_2]_2$,[4] $[Pd(dpt)_2]_2$,[4] and $[Cu(dpt)]_2$[5] confirmed that the triazenide ligand actually bridges the metal centers in these compounds. The first compound to be shown to have a bidentate triazenide coordinated to a single metal atom was $Co(dpt)_3$.[6] The structures of two different crystalline forms have been reported (the first with toluene solvate[6,7] and the other unsolvated[8]), and both confirm the presence of the four-membered $\overline{\mathrm{M{-}N{-}N{-}N}}$ ring. Very recently, synthetic work has been reported on organometallic complexes of second- and third-row transition metals containing triazenido ligands.[9-17] These workers have deduced both bridging and bidentate bonding modes for the triazenido ligand in these complexes. We present here the structure of one such complex, *trans*-$Ru(H)(dtt)(CO)(PPh_3)_2$[9a] (dtt = 1,3-di-*p*-tolyltriazenido, Ph = C_6H_5) in which the dtt ligand is coordinated to the metal in a bidentate fashion.[18]

Table I. Crystal Data for *trans*-[Ru(H)(dtt)(CO)$(PPh_3)_2$]

Mol formula	$C_{51}H_{45}N_3OP_2Ru$
Mol wt	878.96 amu
Cell constants[a]	a = 14.074 (2) Å b = 15.264 (3) Å c = 12.195 (2) Å α = 109.78 (1)° β = 111.74 (1)° γ = 65.03 (1)° V = 2154 Å^3
Space group	C_i^1-$P\bar{1}$
Z	2
Density	1.35 (calcd), 1.34 (exptl) g cm^{-3}
Crystal dimensions	0.521 × 0.452 × 0.173 mm
Crystal vol	1.16 × 10^{-2} mm^3
Absorption coeff, μ[a]	40.29 cm^{-1}

[a] Cu Kα_1 (λ 1.540 562 Å) at 22 °C ambient temperature.