

THE CRYSTAL, MOLECULAR STRUCTURE AND EPR SPECTRUM OF DIPOTASSIUM BIS[(μ -ISOTHIOCYANATO-N,S)-(N-SALICYLIDENE-(R)-PHENYLALANINATO)(N-SALICYLIDENE-(S)-PHENYLALANINATO)]-DICUPRATE(II)

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The title compound crystallizes in the triclinic system with a space group of $P\bar{1}$ (No. 2); $a = 0.8283(4)$, $b = 0.9477(6)$, $c = 1.2271(5)$ nm; $\alpha = 74.251(41)$, $\beta = 82.351(34)$, $\gamma = 70.475(40)^\circ$, $V = 0.87282(74)$ nm³, $Z = 1$, $F(000) = 432$, $\mu = 1.624$ mm⁻¹, room temperature. The structure was refined to $R = 0.0571$ ($R_w = 0.0568$) for 1 920 observed reflections. The Cu(II) adopts a distorted square-pyramidal coordination. The base of the coordination polyhedron is formed by O(1), N(1), O(2) donor atoms of the terdentate Schiff-base dianion (sal-(R)-phe or sal-(S)-phe) and N(2) atom of the additional NCS⁻ ligand. The axial site (apical position) of the pyramid is occupied by a weakly bonded S-atom; Cu-S = 0.2995(1) nm, originating from the -NCS- bridging ligands. Two units, [Cu(sal-(R)-phe)(NCS)]⁻ and the corresponding (S)-form, are thus joined into centrosymmetric dicuprate complex anion; [Cu₂(μ -isothiocyanato-N,S)₂(sal-(R)-phe)(sal-(S)-phe)]²⁻. The Q-band EPR spectrum of this complex (powdered sample, room temperature) exhibits orthorhombic g components: $g_z = 2.234$, $g_y = 2.059$ and $g_x = 2.039$ which can be interpreted as molecular ones ($G = 4.9$).

Cu(II) complexes of terdentate Schiff bases of the N-salicylideneaminoalkanoate type (denoted by TSB) have received considerable attention in view of their interest in many fields of bioinorganic chemistry. For example, many compounds of this group have been shown to exhibit antimicrobial¹ and SOD-like (ref.²) activities; recently, a copper(II)-TSB chelate formation has been investigated as a tool for intermolecular cross-linking and immobilization of proteins³. Of special importance is that these complexes serve as valuable models for the more complicated metal-vitamin B₆ - amino acid systems, which are known to be intermediates in the enzymatically catalyzed metabolic reactions of amino acids^{4,5}.

Another point of interest in the Cu(II)-TSB complexes is the coordination geometry around the metal ion. Previous studies have shown^{4,6-13} that the TSB ligands form many complexes with Cu(II) that show a variety of stoichiometries and structures depending on the preparation conditions. If an additional monodentate ligand

(denoted by L) is present in the reaction mixture, square-pyramidal complexes of composition $[\text{Cu}^{\text{II}}(\text{TSB})\text{L}]$ are usually formed, with L occupying the fourth basal-plane coordination site. The axial site of the coordination polyhedron (apical position) is occupied either by a weakly bonded H_2O molecule^{7,9} or by a suitable donor atom from the neighbouring complex molecule, which leads to the formation of dimeric units^{8,9,12,13} or even to the polymeric structure^{4,6,11}. On the other hand, when L is absent, the antiferromagnetically coupled dimeric complexes $[\text{Cu}_2(\text{TSB})_2]$ (the Cu atoms bridged by the phenolic O atom) are often formed¹⁴⁻¹⁷.

Recently, complexes of the stoichiometry $\text{M}[\text{Cu}(\text{TSB})(\text{NCS})] \cdot x\text{H}_2\text{O}$ or $\text{Na}_2[\text{Cu} \cdot (\text{sal-}\beta\text{-ala})(\text{NCS})](\text{NCS}) \cdot 2\text{H}_2\text{O}$ (where $\text{M} = \text{Na}^+$, K^+ or NH_4^+ ; $x = 0, 1, 2$; sal- β -ala = N-salicylidene- β -alaninate), consisting of the anionic $[\text{Cu}^{\text{II}}(\text{TSB})(\text{NCS})]^-$ species (present as dimeric units) have been identified in the solid state^{12,13,18}. The title complex belongs to the latter type of Cu(II) complexes and its structural analysis and Q-band EPR spectral study were undertaken in continuation of our studies on the structure of $[\text{Cu}^{\text{II}}(\text{TSB})]$ complexes. Preliminary findings on the structure and X-band (EPR) spectral study have been reported¹².

EXPERIMENTAL

The complex $\text{K}[\text{Cu}(\text{C}_{16}\text{H}_{13}\text{NO}_3)(\text{NCS})]$ was prepared as described in ref.¹⁸. It crystallizes from the reaction mixture in aqueous ethanol, forming well developed dark green-blue crystals. For $\text{C}_{17}\text{H}_{13}\text{CuKN}_2\text{O}_3\text{S}$ (428.0) calculated: 47.70% C, 3.06% H, 6.54% N; found: 47.45% C, 2.99% H, 6.43% N.

The EPR spectrum of the powdered sample was recorded at room temperature in Q-band (35.1 GHz) on an ERS-200 spectrometer (G.D.R.). DPPH was used as an internal standard.

The crystal used for data collection had approximately octahedral shape with dimensions $0.1 \times 0.15 \times 0.2$ mm. The experimental density (measured by flotation in bromoform — cyclohexane) is 1.620(10); the calculated value is 1.628 kg m^{-3} . Weissenberg photographs did not exhibit any symmetry. The lattice parameters were found by using the program UB (ref.¹⁹) and refined diffractometrically from the positional angles of 14 reflections, $3^\circ < 2\theta < 15^\circ$. The intensity measurements were carried out by using a Syntex P2₁ diffractometer and a graphite-monochromated MoK_α radiation.

Correction for Lorentz and polarization factors was performed by using the program XP21 (ref.²⁰), corrections for absorption and extinction were neglected. The structure was solved by the heavy-atom method in the $P\bar{1}$ space group by using the program XFPS (ref.²¹). Refinement was made on $|F_o|$ by a block-diagonal least-squares method, anisotropic thermal parameters for the heavier atoms, hydrogen atoms fixed in calculated positions ($B = 0.03$ to 0.06 nm^2), the weighting scheme $w^{-1} = \sigma^2(F) + (0.02|F_o|)^2$, where $\sigma(F)$ was derived from pulse statistics; in the last cycle $(\Delta/\sigma)_{\text{max}} = 0.059$, $(\Delta\rho)_{\text{max}} = 560$, $(\Delta\rho)_{\text{min}} = -590 \text{ e nm}^{-3}$. The final crystallographic coordinates of the non-hydrogen atoms are given in Table I,* the bond distances in Table II and bond angles in Table III. All calculations were performed with the XRC83 program system²² on an ES 1 045-01 computer.

* Anisotropic thermal parameters, H-atom coordinates and F_o/F_c tables are available at the authors.

RESULTS AND DISCUSSION

Description of the Structure

The crystal structure of the title compound can be described as consisting of dimeric units, $[\text{Cu}_2(\text{sal-(R)-Phe})(\text{sal-(S)-Phe})(\mu\text{-NCS})_2]^{2-}$ (where sal-Phe is N-salicylidene-phenylalanine), charge of which being compensated by K^+ ions (Fig. 1). The dimerization of the Schiff base complexes (related by a centre of symmetry at $1/2, 0, 0$) occurs via a semi-coordinate $\text{Cu}(1)\text{—S}(1^i)$ ($i: 1 - x, -y, -z$) bond at a long distance of $0.2995(1)$ nm. The length of this bond is comparable to that found in related complexes containing apically bonded (s)-ligands, e.g. thiourea or its analogues²³. Thus,

TABLE I

Final atomic coordinates ($\cdot 10^4$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters B_{eq} ; $B_{\text{eq}} = (4/3) \sum_i \sum_j B_{ij} a_i a_j$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}, \text{Å}^2$
Cu(1)	1867.9(4)	363.6(3)	627.1(3)	2.59(1)
S(1)	5616(1)	439(1)	−2412(1)	3.79(3)
O(1)	769(2)	2361(2)	883(1)	3.28(5)
O(2)	2902(2)	−1664(2)	320(1)	3.23(4)
O(3)	2931(2)	−4094(2)	897(1)	3.99(7)
N(1)	405(2)	−613(2)	1679(1)	2.28(5)
N(2)	3224(3)	1202(2)	−679(2)	3.33(8)
C(1)	2346(3)	−2738(2)	945(2)	2.69(8)
C(2)	896(3)	−2297(2)	1832(2)	2.61(8)
C(3)	−990(3)	99(2)	2170(2)	2.38(8)
C(4)	−1541(3)	1736(2)	2132(2)	2.27(7)
C(5)	−3067(3)	2285(3)	2756(2)	3.15(8)
C(6)	−3712(3)	3813(3)	2791(2)	3.78(10)
C(7)	−2846(3)	4820(3)	2173(2)	3.86(10)
C(8)	−1341(3)	4332(2)	1541(2)	3.21(8)
C(9)	−649(3)	2763(2)	1500(2)	2.82(7)
C(10)	4202(3)	876(2)	−1403(2)	2.54(7)
C(11)	1557(3)	−3199(3)	3012(2)	3.20(8)
C(12)	209(3)	−2923(2)	3956(2)	2.90(8)
C(13)	−1244(4)	−3399(3)	4040(2)	3.75(9)
C(14)	−2549(4)	−3057(3)	4856(2)	4.99(10)
C(15)	−2396(4)	−2276(4)	5622(2)	6.01(13)
C(16)	−971(4)	−1842(3)	5565(2)	5.82(12)
C(17)	330(4)	−2147(3)	4737(2)	4.45(11)
K	3961(1)	3166(1)	594(1)	3.70(3)

TABLE II

Interatomic distances (nm) in $K_2[Cu_2(\text{sal}(\text{R})\text{-phe})(\text{sal}(\text{s})\text{-phe}(\text{NCS})_2]$ (standard deviations are in parentheses)

Atoms	Bond length	Atoms	Bond length
Cu(1)–N(1)	0·1917(2)	C(3)–C(4)	0·1452(3)
Cu(1)–O(1)	0·1899(2)	C(4)–C(5)	0·1404(3)
Cu(1)–O(2)	0·1943(2)	C(4)–C(9)	0·1419(3)
Cu(1)–N(2)	0·1972(2)	C(5)–C(6)	0·1376(3)
Cu(1)–S(1 ¹)	0·2995(8)	C(6)–C(7)	0·1386(4)
S(1)–C(10)	0·1625(2)	C(7)–C(8)	0·1386(4)
O(1)–C(9)	0·1311(3)	C(8)–C(9)	0·1416(3)
O(2)–C(1)	0·1277(3)	C(11)–C(12)	0·1511(3)
C(12)–C(13)	0·1403(4)	C(12)–C(17)	0·1387(4)
O(3)–C(1)	0·1228(3)	C(13)–C(14)	0·1389(4)
N(1)–C(2)	0·1474(3)	C(14)–C(15)	0·1385(4)
N(1)–C(3)	0·1291(3)	C(15)–C(16)	0·1361(5)
N(2)–C(10)	0·1154(3)	C(16)–C(17)	0·1392(4)
C(1)–C(2)	0·1583(3)	C(2)–C(11)	0·1535(3)

TABLE III

The bond angles (°) in $K_2[Cu_2(\text{sal}(\text{R})\text{-phe})(\text{sal}(\text{s})\text{-phe}(\text{NCS})_2]$ (standard deviations are in parentheses)

Atoms	Bond angle	Atoms	Bond angle
O(1)–Cu(1)–O(2)	177·2(1)	O(2)–C(1)–O(3)	123·9(2)
O(1)–Cu(1)–N(1)	95·5(1)	O(2)–C(1)–C(2)	117·3(2)
O(1)–Cu(1)–N(2)	91·0(1)	O(3)–C(1)–C(2)	118·7(2)
O(1)–Cu(1)–S(1)	92·2(1)	N(1)–C(2)–C(1)	107·4(2)
O(2)–Cu(1)–N(1)	83·9(1)	N(1)–C(2)–C(11)	112·7(2)
O(2)–Cu(1)–N(2)	89·1(1)	C(1)–C(2)–C(11)	108·3(2)
O(2)–Cu(1)–S(1)	90·5(1)	N(1)–C(3)–C(4)	124·4(2)
N(1)–Cu(1)–N(2)	168·3(1)	C(3)–C(4)–C(5)	115·9(2)
N(1)–Cu(1)–S(1)	91·4(1)	C(3)–C(4)–C(9)	123·8(2)
N(2)–Cu(1)–S(1)	98·0(1)	O(1)–C(9)–C(4)	124·6(2)
Cu(1)–O(1)–C(9)	125·6(2)	O(1)–C(9)–C(8)	117·8(2)
Cu(1)–O(2)–C(1)	116·1(2)	S(1)–C(10)–N(2)	178·3(2)
Cu(1)–N(1)–C(2)	114·7(1)	C(2)–C(11)–C(12)	113·2(2)
Cu(1)–N(1)–C(3)	125·2(2)	C(11)–C(12)–C(13)	120·4(2)
C(2)–N(1)–C(3)	119·9(2)	C(11)–C(12)–C(17)	121·6(2)
Cu(1)–N(2)–C(10)	143·3(2)		

the coordination sphere of the copper atom can be described as an elongated square pyramid, the four basal atoms being O(1), N(1), and O(2) of the Schiff-base ligand and the thiocyanate N atom. A neighbouring complex anion provides the apical S atom to complete the pyramidal 4 + 1 coordination.

The Cu—Cu distances within the crystal structure indicate no interaction between the metal ions: the intradimer Cu(1)—Cu(1ⁱ) (ⁱ: 1 - x, -y, -z) separation is 0.50820(5) nm and the shortest Cu(1)—Cu(1ⁱⁱ) (ⁱⁱ: -x, -y, -z) distance is 0.39610(5) nm.

The in-plane copper–ligand bond lengths range from 0.1899 to 0.1972 nm; these values agree well with those found in similar [Cu^{II}(TSB)L] or [Cu^{II}(TSB)(NCS)]⁻ complexes^{4,6-13}, with the exception of the compound [Cu(salgly)(H₂O)].0.5 H₂O (refs^{4,6}) (salgly is N-salicylidene-glycinate) in which the in-plane Cu—OH₂ distance of 0.2016 nm is somewhat longer compared to the corresponding Cu—NCS bond in the present complex (especially if the different covalent radii of the O- and N-donor atoms are taken into account).

Data on the least-squares planes through the individual rings of the complex anion are given in Table IV. The six-membered chelate ring of the salicylaldimino moiety is almost planar with small puckering toward the half-chair. The five-membered chelate ring [Cu(1), O(2), C(1), C(2), N(1)] is also approximately planar, with the distortion from planarity towards an intermediate between an N(1)-envelope and C(1), C(2)-twist conformations. The C(β) atom of the phenylalaninato moiety

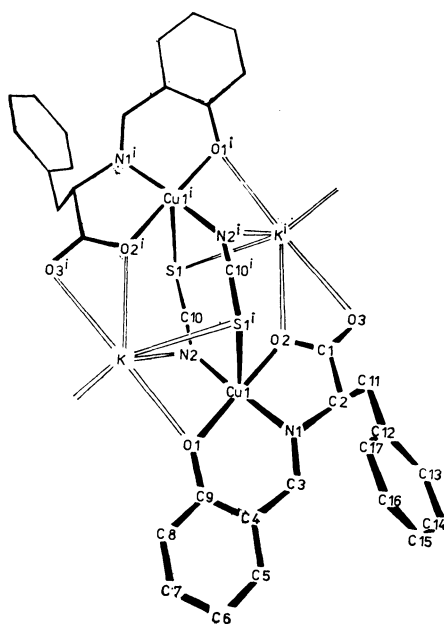


FIG. 1

A perspective view of the dimeric anion, [Cu₂(sal-R-phe)(sal-S-phe)(μ-NCS)₂]²⁻, showing its contacts with K⁺ ions and the atom numbering

occupies a pseudoaxial position with respect to the five-membered ring. The maximum deviations from the least-squares planes are: the six-membered chelate ring 0.0080(2), five-membered one 0.0069(2), the phenyl ring of the salicylaldimine 0.0006(2), and the phenyl ring of the amino-acid moiety 0.0012(3) nm.

The mean plane of the six-membered chelate ring forms an angle of 3.1° with respect to the phenyl ring of the salicylaldiminato moiety and an angle of 49.7° with respect to the phenyl ring of the amino-acid portion of the molecule. The dihedral angle between the six-membered and five-membered chelate rings has the value of 5.7°. The valence angle within the NCS group is 178.3°.

Besides the weak apical copper(II)–sulphur bond, no hydrogen bonding was observed in the crystal structure. The packing is dominated by Coulombic interactions between K⁺ ions and the heteroatoms of the neighbouring dimeric anions, which leads to the formation of chains extending throughout the structure (Fig. 2). The chains are held together by van der Waals forces and by π – π interactions between

TABLE IV

The deviations of atoms from the least-squares planes, d , in the crystal structure of K₂[Cu₂(sal-(R)-phe)(sal-(S)-phe)·(NCS)₂] (standard deviations are in parentheses)

Atom	d , nm	Atom	d , nm
Six-membered chelate ring			
Cu(1)	0.00020(3)	N(1)	–0.0080(2)
C(3)	0.0036(2)	C(4)	0.0053(2)
C(9)	0.0010(2)	O(1)	–0.0052(2)
Five-membered chelate ring			
Cu(1)	–0.00010(3)	O(2)	0.0036(2)
C(1)	–0.0022(2)	C(2)	–0.0069(2)
N(1)	0.0060(2)		
Phenyl ring			
C(4)	–0.0004(2)	C(5)	0.0006(2)
C(6)	–0.0006(3)	C(7)	0.0002(3)
C(8)	–0.0001(3)	C(9)	0.0002(2)
Phenylalaninate ring			
C(12)	0.0007(2)	C(13)	–0.0012(3)
C(14)	0.0008(3)	C(15)	0.0004(3)
C(16)	–0.0009(3)	C(17)	0.0000(3)

the phenyl rings. The coordination number of K^+ is 6, with the distances to N(2), O(1), O(2ⁱ), O(3ⁱ), S(1ⁱ) and O(3ⁱⁱ) (ⁱ: 1 - x, -y, -z; ⁱⁱ: -x, -y, -z) atoms 0.2977(3), 0.2941(3), 0.2767(3), 0.3183(3), 0.3470(3) and 0.2563(3) nm, respectively.

EPR Spectrum

Previous measurement¹² of the EPR spectrum of the title compound, taken from powdered sample at X-band frequency, revealed an axial symmetry (with $g_{\parallel} > g_{\perp}$), a result inconsistent with the crystalstructure analysis. Therefore, a possibility was considered that the sensitivity of the experimental technique used was too low to resolve potential splitting of the in-plane g -components. Indeed, the EPR spectrum recorded at Q-band frequency is clearly orthorhombic: the g -values are: $g_z = 2.234$, $g_y = 2.059$, $g_x = 2.039$; $\bar{g} = 2.110$ [$\bar{g} = (g_x + g_y + g_z)/3$].

From these experimental g -values a parameter $G = 4.9$ can be computed $G = (g_{\parallel} - g_0)/(g_{\perp} - g_0)$; $g_{\parallel} = g_z$, $g_{\perp} \approx (g_x + g_y)/2$, $g_0 = 2.002$, indicating that the experimental g -values represent the molecular ones. This result is in agreement with

TABLE V
The some selected [Cu(salgly)L] and their axial Cu(II)—O distances and \bar{g} -values

Cu(salgly)L L	Cu—O axial distance, nm	\bar{g} -value
H ₂ O ^a	0.2308	2.136
2-Methylimidazole ^b	0.2481	2.125
Thiourea ^c	0.2771	2.106

^a Ref.⁴; ^b ref.¹¹; ^c ref.⁸.

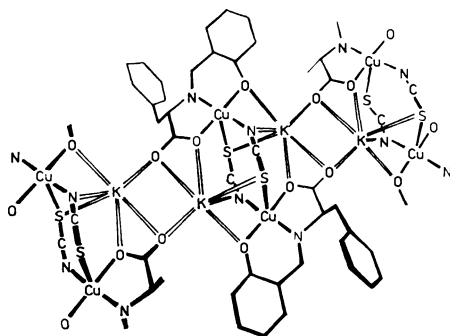


FIG. 2

A perspective view on a chain segment of the crystal structure realized by the dimeric cuprate anions in contacts with the K^+ cations. The chains are oriented in the crystal structure on parallel lines and packed via π - π interactions of their coplanar aligned parts

the structural analysis results which show a ferrodistorptive ordering of the complex anions within the dimer as well as the co-planar alignment of the dimers within the structure.

However, the value of the parameter G (4.9) is somewhat higher when compared with the values (4.6 ± 0.2) commonly observed for ferrodistorptively ordered Cu(II) complexes of this type²⁴. Such an increase in the parameter G has been attributed to the effect of "out-of-plane" π -bonding.

The somewhat small average g -value ($\bar{g} = 2.110$) for the title complex most likely reflects the large distance of the apically bonded S-donor atom as well as the increased covalency in the Cu—NCS equatorial bond as compared, for example, to that in a Cu—OH₂ bond. This interpretation is also supported by the position of the band due to $d-d$ transition in the electronic spectrum of the present complex ($16\,230\text{ cm}^{-1}$) (ref.¹⁸).

The effect on the g -values of the above-discussed phenomena (variations in the amount of the axial distortion and the covalency in the in-plane Cu—ligand bond) is obvious from the data of Table V in which three congeneric [Cu(salgly)L] complexes are compared. As can be seen from the table, the \bar{g} -value for the present complex is very close to that reported for [Cu(salgly)(tu)] (where tu means thiourea). These data suggest that the strengths of the apical contacts in the latter two complexes (Cu—O^{ap} = 0.2771 and Cu—S^{ap} = 0.2995 nm) are comparable (taking into account the larger covalent radius of the S-donor atom).

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