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Synthesis, Thermal, Magnetic Properties and Crystal Structure of Homodinuclear Copper(II) Complexes with New 'End-off' Compartmental Schiff Bases

P. GUERRIERO, U. CASELLATO, D. AJO', S. SITRAN, P. A. VIGATO*
Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti 4, I-35020 Padua, Italy
and R. GRAZIANI
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell' Universita', Via Loredan 4, I-35100 Padua, Italy

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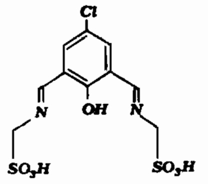
Abstract

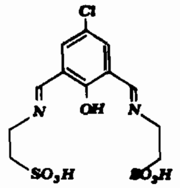
The homodinuclear copper(II) complex $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$ (H_5L_C is the Schiff base derived from the condensation of 2,6-diformyl-4-chlorophenol and (∓)1-aminoethanephosphonic acid in a 1:2 molar ratio) has been prepared and characterized by IR, UV data, scanning electron microprobe analysis and X-ray diffraction. The crystal structure of $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$ has been determined by X-ray crystallography and refined to the final R of 0.032. The compound is triclinic, space group $P\bar{1}$, with $a = 17.129(5)$, $b = 11.558(5)$, $c = 8.372(5)$ Å, $\alpha = 95.95(3)$, $\beta = 104.72(3)$, and $\gamma = 76.21(3)°$; $Z = 2$. The compound is a dinuclear complex in which the copper ions are five-coordinate square pyramidal. One oxygen atom from the pentadentate pentaanionic ligand and the OH^- oxygen provide bridging of the metal ions. Two water molecules are in the apical positions. The sodium ions are octahedrally surrounded by oxygen atoms from water and phosphonate groups. Selected bond distances are: Cu–O(base) 1.92 to 1.98 Å; Cu–N 1.97 Å; Cu–O(axial) 2.51 and 2.28 Å; Na–O(water) 2.38 to 2.50 Å; Na–O(phosphonate) 2.57 Å. The crystal lattice is stabilized by an extensive network of hydrogen bonds. The thermal and magnetic behaviour over 68–290 K temperature range are reported together with a comparison with the analogous homodinuclear copper(II) complex with the ligand H_3L_A (H_3L_A is the Schiff base derived from the condensation of 2,6-diformyl-4-chlorophenol and aminomethanesulphonic acid in a 1:2 molar ratio). The two copper(II) ions exhibit a significant antiferromagnetic interaction ($J = -202.5$ cm^{-1}).

Introduction

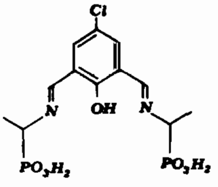
In previous papers [1, 2] we have reported the synthesis and the correlation between structural and magnetic properties of a series of transition metal complexes with 'end-off' compartmental Schiff bases, (H_3L_A, H_3L_B, H_5L_C and H_5L_D) derived from the condensation of 2,6-diformyl-4-chlorophenol and α- or β-aminosulphonic or the analogous phosphonic acids



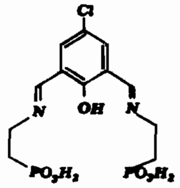
H_3L_A



H_3L_B

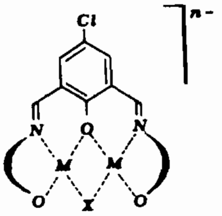


H_5L_C



H_5L_D

The homodinuclear complexes have been obtained by template or step by step procedures; the dinuclear unit shows an endogenous phenolate oxygen while the exogenous group X is –OH or –Cl.



In particular the crystal structure of the copper $Cu_2(L_A)OH$ complex, grown from dimethylsulphoxide, has evidenced the compound must be correctly formulated as a centrosymmetric dimer, {[Cu_2L_A-

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*Author to whom correspondence should be addressed.

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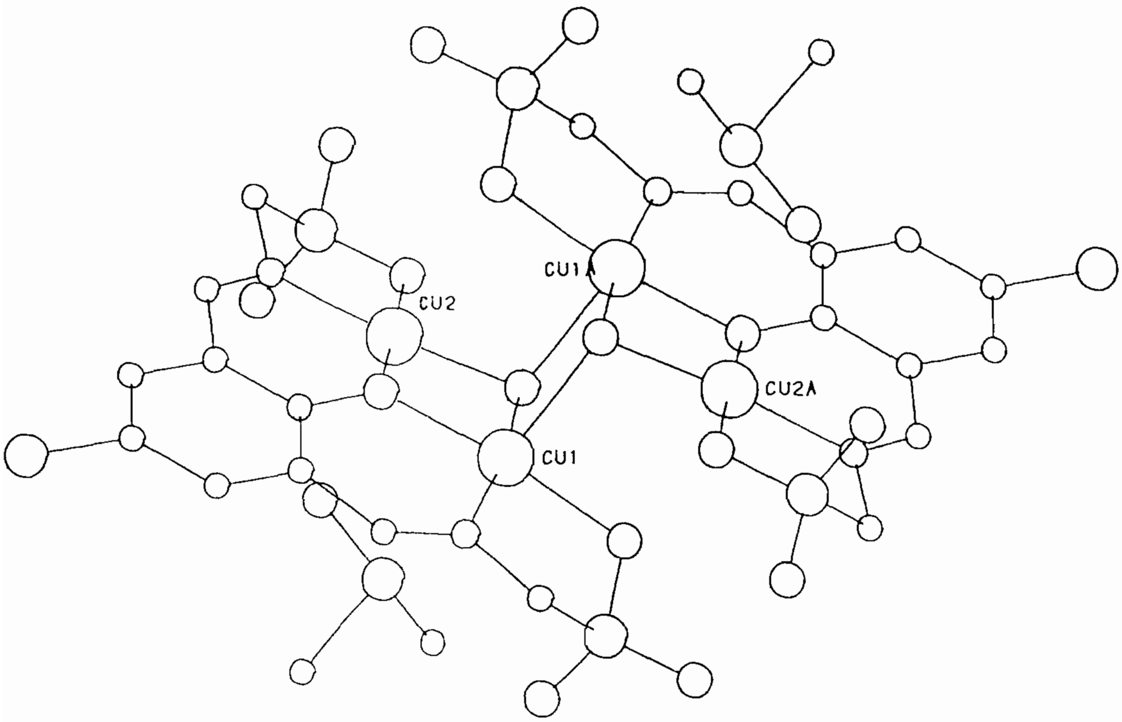

$(OH)(H_2O)](dmso)\}_2$, formed by two binuclear units approximately parallel and linked to each other by one –OH group [2].

In the asymmetric unit one copper atom is five coordinated in a square pyramidal arrangement, the other one is square planar.

In this complex the copper ions are antiferromagnetically coupled ($J = -173.7$ cm^{-1}). In the similar phosphonato complex, $Na_2Cu_2L_DOH$ [2] an antiferromagnetic behaviour was also observed; however the high amount of paramagnetic impurities ($\simeq 12.5\%$) and the uncertainty about the number of water molecules prevented a correct evaluation of its magneto–structural correlation. We report here the thermal and magnetic behaviour of the complex $Na_2Cu_2L_COH \cdot 13H_2O$ together with its X-ray structure. A comparison with the tetranuclear complex $\{[Cu_2L_AOH(H_2O)](dmso)\}_2$ is also reported.

Experimental

2,6-diformyl-4-chlorophenol was prepared according to the literature [3, 4]; (∓)1-aminoethanephosphonic acid was a commercial product (Aldrich). The synthesis of the sodium salt of the ligand H_5L_C was carried out as already reported [2].

Preparation of $Na_2Cu_2L_COH \cdot 13H_2O$

To a methanolic solution of the ligand salt (Na_5L_C) (1 mmol), $Cu(OAc)_2 \cdot 4H_2O$ (2 mmol), in water, was added. The solution that immediately turned deep green, was refluxed for 1 h, then reduced in volume. The precipitate obtained was cooled, filtered, washed with methanol, diethylether and dried *in vacuo*. The same complex has been obtained by using the sodium salt of the ligand freshly prepared '*in situ*'.

Well formed single crystals were obtained by slow evaporation of the mother liquors or by addition of ethanol to this solution. *Anal.* Calc. for $Na_2Cu_2C_{12}H_{13}O_8ClP_2 \cdot 13H_2O$: C, 17.62; H, 4.81; N, 3.42. Found: C, 17.37; H, 4.42; N, 3.27%.

Sodium, copper, chlorine and phosphorous ratios were found to be approximately 2:2:1:2 within the standard error by integration of back-scattered X-rays using a scanning electron microprobe [2].

Physical Measurements

The IR spectra were carried out as KBr pellets using a Perkin-Elmer 580B model Infrared Spectrophotometer. Electronic spectra were carried out as nujol mulls, at room temperature using a Cary 17D model Spectrophotometer. Magnetic susceptibilities were determined by the Faraday method at room and at variable temperature over the 68–290 K temperature region, the apparatus (Oxford Instruments) being calibrated with $HgCo(NCS)_4$ [5]. Diamagnetic corrections were carried out [6]. The thermogravimetric and differential thermoanalysis curves were obtained using Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min^{-1}; heating rate 5 min^{-1}) and in air under the same conditions. Neutral alumina (C. Erba product) was used as reference material.

X-ray Data

A crystal fragment of maximum dimension 0.2 mm was used for the X-ray work. Crystal data are: $C_{12}H_{39}N_2O_{21}ClP_2Na_2Cu_2$, formula weight = 817.6, $a = 17.129(5)$, $b = 11.558(5)$, $c = 8.372(5)$ Å, $\alpha = 95.95(3)$, $\beta = 104.72(3)$, and $\gamma = 76.21(3)^\circ$, $V = 1555$ Å^3, $D_c = 1.75$ g cm^{-3} for $Z = 2$, μ(Mo Kα) = 66 cm^{-1}, triclinic, space group $P\bar{1}$.

The intensities of 4975 reflexions were measured up to $\theta = 25^\circ$ on a Philips four-circle diffractometer with the $\theta/2\theta$ technique using graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). The compound remained stable under irradiation. The measured intensities were corrected for Lp and for absorption [7], and 3862 independent reflexions with $I > 3\sigma(I)$ were considered as 'observed' and used in subsequent calculations. The structure was solved by standard methods and refined to the conventional R factor of 0.032 when the maximum shift on the refined parameters was 0.2σ. Ring carbon atoms were refined as rigid bodies (C–C = 1.395 Å) together with their attached hydrogen atoms. The positions of the other hydrogen atoms were determined from Fourier difference electron density maps. The quantity minimized in the refinement was $\Sigma w \Delta F^2$ with $w = 1$. Scattering factors were taken from ref. 8. Final atomic parameters are listed in Table I, bond distances and angles are in Tables II and III. All calculations were performed using the SHELX program system [9].

TABLE I. Atomic Parameters for $Na_2[Cu_2L_COH(H_2O)_2] \cdot 11H_2O$

Atom	*x/a*	*y/b*	*z/c*
Atomic coordinates			
Cu1	0.76565(3)	0.58154(5)	−0.10595(7)
Cu2	0.77373(3)	0.34923(4)	0.02531(7)
P1	0.80980(7)	0.71319(9)	−0.33329(14)
O1	0.84451(18)	0.65678(27)	−0.16353(38)
O2	0.81148(19)	0.62282(26)	−0.47622(40)
O3	0.84813(18)	0.81720(25)	−0.34665(37)
P2	0.82405(7)	0.14098(10)	0.23702(14)
O4	0.85715(18)	0.22813(26)	0.15829(39)
O5	0.87442(21)	0.01527(28)	0.22522(46)
O6	0.81653(23)	0.18168(32)	0.40962(43)
O7	0.69001(17)	0.48019(26)	−0.09043(40)
O8	0.84338(18)	0.45813(26)	0.02447(38)
O9	0.80698(23)	0.25386(32)	−0.20681(43)
O10	0.73166(25)	0.69823(36)	0.14479(53)
Cl1	0.33485(7)	0.52296(12)	−0.37009(18)
C1	0.70133(27)	0.77638(39)	−0.32754(60)
N1	0.67492(22)	0.68224(31)	−0.26068(46)
C2	0.60021(27)	0.67120(38)	−0.30962(59)
C9	0.61110(26)	0.29640(39)	−0.03433(58)
N2	0.68856(22)	0.26229(33)	0.02741(47)
C10	0.72079(31)	0.14339(45)	0.10233(74)
C11	0.64738(46)	0.81392(68)	−0.50317(109)
C111	0.70594(80)	0.87913(105)	−0.18457(170)
C12	0.66617(53)	0.09031(88)	0.16044(129)
C121	0.71069(85)	0.04554(102)	−0.00781(180)
C4	0.48004(14)	0.59308(21)	−0.32430(34)
C5	0.44040(14)	0.50903(21)	−0.29137(34)
C6	0.48547(14)	0.41401(21)	−0.19258(34)
C7	0.57019(14)	0.40304(21)	−0.12671(34)
C8	0.60983(14)	0.48710(21)	−0.15963(34)
C3	0.56475(14)	0.58212(21)	−0.25843(34)
Na1	1.00531(10)	0.31092(14)	−0.32202(21)
O11	0.99206(20)	0.29249(29)	−0.61650(41)
O12	0.96705(21)	0.11996(30)	−0.32734(45)
O13	1.14826(21)	0.18905(29)	−0.30871(45)
O14	0.99571(21)	0.33017(30)	−0.04312(41)
O15	1.07339(21)	0.46456(30)	−0.33261(39)
O16	0.85654(20)	0.38422(29)	−0.40470(44)

(continued)

TABLE I. *(continued)*

Atom	x/a	y/b	z/c
Atomic coordinates			
Na2	0.94208(10)	0.14967(15)	−0.05741(21)
O17	0.75125(22)	0.06226(33)	0.58347(48)
O18	0.92057(20)	−0.05028(30)	−0.06998(44)
O19	0.43578(30)	0.16580(41)	−0.04339(65)
O20	0.50973(28)	−0.01203(46)	0.75434(61)
O21	0.42303(29)	0.88153(46)	0.46142(64)
Hydrogen coordinates			
H2	0.5579(32)	0.7273(47)	−0.3921(63)
H4	0.4451(1)	0.6666(2)	−0.4007(3)
H6	0.4547(1)	0.3489(2)	−0.1670(3)
H9	0.5750(32)	0.2442(46)	−0.0115(62)
H81	0.8614(35)	0.4778(50)	0.1066(69)
H91	0.8138(33)	0.2959(50)	−0.2743(69)
H92	0.7828(34)	0.2089(50)	−0.2630(68)
H101	0.7661(36)	0.7354(52)	0.1706(71)
H102	0.7248(35)	0.6702(51)	0.2187(72)
H111	0.9574(33)	0.2690(47)	−0.6764(67)
H112	1.0303(34)	0.2678(48)	−0.6411(67)
H121	0.9980(35)	0.0772(50)	−0.3406(72)
H122	0.9312(33)	0.1125(46)	−0.4111(66)
H131	1.1488(31)	0.1806(44)	−0.4186(69)
H132	1.1448(31)	0.1220(49)	−0.2820(63)
H141	0.9583(33)	0.3769(48)	−0.0242(66)
H142	1.0295(34)	0.3394(48)	0.0246(69)
H151	1.0519(31)	0.5382(49)	−0.3630(63)
H152	0.9058(37)	0.5579(54)	−0.6127(71)
H161	0.8395(33)	0.4454(50)	−0.4295(68)
H162	0.8414(34)	0.3545(50)	−0.4825(68)
H171	0.7823(33)	0.0007(49)	0.6117(66)
H172	0.7763(31)	0.0854(46)	0.5141(65)
H181	0.8991(34)	−0.0759(49)	−0.1434(69)
H182	0.8955(32)	−0.0412(45)	0.0109(66)
H191	0.4264(41)	0.1296(56)	−0.0043(83)
H192	0.3782(33)	0.2042(45)	−0.0887(63)
H201	0.4762(33)	0.0354(48)	0.8095(66)
H202	0.4696(33)	0.9537(46)	0.6837(66)
H211	0.3712(34)	0.9033(46)	0.4558(65)
H212	0.4312(37)	0.9173(52)	0.4014(72)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters ($U(ij) \times 10^{-4}$)[a]						
Cu1	180(3)	216(3)	295(3)	77(2)	8(2)	−58(2)
Cu2	174(3)	190(3)	276(3)	66(2)	−3(2)	−51(2)
P1	187(5)	191(5)	276(7)	38(5)	50(5)	−47(4)
O1	214(15)	356(18)	313(18)	121(15)	−16(14)	−113(13)
O2	332(18)	210(16)	389(20)	−21(14)	121(15)	−43(13)
O3	266(16)	225(15)	312(18)	40(13)	62(14)	−96(13)
P2	216(5)	195(5)	245(6)	48(5)	18(5)	−53(4)
O4	229(16)	278(16)	365(19)	136(14)	−10(14)	−72(13)
O5	364(19)	235(17)	551(24)	73(16)	123(18)	−13(14)
O6	549(23)	478(22)	342(21)	−11(17)	140(18)	−211(18)
O7	139(14)	229(16)	410(20)	115(14)	−16(14)	−43(12)
O8	225(16)	214(15)	243(17)	38(14)	−4(14)	−68(12)

(continued)

TABLE I. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters ($U(ij) \times 10^{-4}$)[a]						
O9	449(22)	348(20)	288(20)	−38(16)	104(17)	−118(16)
O10	435(23)	430(23)	470(26)	31(19)	75(20)	−111(17)
Cl1	169(5)	515(8)	610(9)	32(7)	−47(6)	−73(5)
Cl	245(23)	236(23)	357(29)	84(21)	105(21)	−14(18)
N1	254(19)	192(18)	295(22)	44(16)	77(17)	−42(15)
C2	217(23)	206(22)	306(27)	56(20)	42(21)	7(18)
C9	228(22)	266(23)	336(27)	44(20)	36(20)	−111(18)
N2	242(19)	241(21)	325(23)	64(17)	−8(17)	−82(16)
C10	329(27)	288(27)	680(40)	211(27)	−140(27)	−156(22)
C11	125(37)	169(39)	296(51)	146(36)	44(35)	31(30)
C111	601(80)	364(66)	765(95)	97(63)	305(73)	−86(58)
C12	155(43)	433(57)	479(65)	322(51)	−45(43)	−165(40)
C121	774(88)	328(60)	893(96)	29(63)	−349(77)	−126(58)
C4	200(21)	265(23)	322(28)	27(20)	19(20)	−16(18)
C5	131(20)	364(26)	368(29)	−9(22)	−18(20)	−54(19)
C6	204(22)	276(24)	375(28)	9(21)	19(20)	−79(18)
C7	206(21)	227(22)	275(27)	21(19)	34(20)	−26(17)
C8	203(21)	215(20)	244(24)	0(18)	52(19)	−47(17)
C3	215(22)	229(22)	268(25)	31(19)	35(19)	−26(18)
Na1	300(9)	293(9)	301(10)	39(7)	65(8)	−64(7)
O11	234(16)	376(18)	334(19)	−45(15)	31(14)	−94(14)
O12	343(19)	364(20)	363(20)	4(16)	62(16)	−26(15)
O13	452(20)	312(18)	367(20)	58(16)	68(17)	−72(15)
O14	293(17)	375(19)	305(19)	−23(15)	31(15)	−32(14)
O15	374(19)	269(17)	275(19)	−7(14)	44(14)	−85(15)
O16	331(18)	256(17)	404(21)	23(15)	35(16)	−33(14)
Na2	307(9)	310(9)	330(10)	38(8)	52(8)	−48(7)
O17	445(21)	406(20)	514(23)	83(17)	162(18)	−118(16)
O18	347(18)	356(18)	333(21)	−28(15)	28(16)	−100(14)
O19	505(25)	579(30)	788(34)	54(24)	164(23)	−88(21)
O20	537(27)	891(36)	696(32)	−89(26)	105(23)	−21(24)
O21	461(24)	824(35)	819(36)	190(26)	58(25)	−53(24)

[a] Anisotropic thermal parameters are in the form $T = \exp -2\,^{2}(U_{ij}H_iH_jA^*_iA^*_j)$.

TABLE II. Bond Distances (Å)[a]

Coordination			
Cu(1)–O(7)	1.977(4)	Cu(2)–O(7)	1.965(4)
Cu(1)–O(8)	1.920(4)	Cu(2)–O(8)	1.933(4)
Cu(1)–O(1)	1.950(4)	Cu(2)–O(4)	1.950(4)
Cu(1)–N(1)	1.975(5)	Cu(2)–N(2)	1.960(5)
Cu(1)–O(10)	2.509(5)	Cu(2)–O(9)	2.278(4)
Ligand			
P(1)–O(1)	1.541(4)	P(2)–O(4)	1.539(4)
P(1)–O(2)	1.507(4)	P(2)–O(5)	1.512(4)
P(1)–O(3)	1.525(4)	P(2)–O(6)	1.498(5)
P(1)–C(1)	1.843(6)	P(2)–C(10)	1.832(7)
C(1)–C(11)	1.57(1)*	C(10)–C(12)	1.45(1)*
C(1)–C(111)	1.61(2)*	C(10)–C(121)	1.42(2)*
C(1)–N(1)	1.474(7)	C(10)–N(2)	1.496(8)
N(1)–C(2)	1.275(7)	N(2)–C(9)	1.284(7)

(continued)

TABLE II. *(continued)*

Ligand			
C(2)–C(3)	1.462(6)	C(9)–C(7)	1.465(6)
C(5)–Cl	1.734(3)	O(7)–C(8)	1.333(5)
Sodium ions			
Na(1)–O(12)	2.452(5)	Na(2)–O(12)	2.399(5)
Na(1)–O(14)	2.382(5)	Na(2)–O(14)	2.462(5)
Na(1)–O(11)	2.423(5)	Na(2)–O(4)	2.566(5)
Na(1)–O(13)	2.503(5)	Na(2)–O(9)	2.435(5)
Na(1)–O(15)	2.376(4)	Na(2)–O(18)	2.421(5)
Na(1)–O(16)	2.438(4)	Na(2)–O(18^{I})	2.396(5)

[a] e.s.d.s given in parentheses refer to the last significant digit. Starred items: Methyl carbon atoms attached to C(1) and C(10) are statistically distributed in the two allowed positions. Accordingly they were refined with an occupancy of 0.5.

TABLE III. Selected Bond Angles (°)[a]

Coordination			
O(1)–Cu(1)–O(8)	98.3(2)	O(4)–Cu(2)–O(8)	97.8(2)
O(1)–Cu(1)–N(1)	89.6(2)	O(4)–Cu(2)–N(2)	89.9(2)
N(1)–Cu(1)–O(7)	89.8(2)	N(2)–Cu(2)–O(7)	91.2(2)
O(7)–Cu(1)–O(8)	80.7(1)	O(7)–Cu(2)–O(8)	80.7(1)
Bridge			
Cu(1)–O(7)–Cu(2)	97.5(2)	Cu(1)–O(8)–Cu(2)	100.6(2)
Ligand			
Cu(1)–O(1)–P(1)	111.7(2)	Cu(2)–O(4)–P(2)	116.0(2)
Cu(1)–N(1)–C(1)	113.2(3)	Cu(2)–N(2)–C(10)	114.7(4)
Cu(1)–N(1)–C(2)	127.3(4)	Cu(2)–N(2)–C(9)	126.7(4)
Cu(1)–O(7)–C(8)	131.7(3)	Cu(2)–O(7)–C(8)	129.9(3)
C(1)–P(1)–O(1)	101.2(2)	C(10)–P(2)–O(4)	103.6(3)
C(1)–P(1)–O(2)	108.5(2)	C(10)–P(2)–O(5)	106.7(3)
C(1)–P(1)–O(3)	107.2(2)	C(10)–P(2)–O(6)	109.9(3)
P(1)–C(1)–N(1)	105.3(4)	P(2)–C(10)–N(2)	108.3(4)
C(1)–N(1)–C(2)	119.5(5)	C(10)–N(2)–C(9)	118.5(5)
N(1)–C(2)–C(3)	125.9(5)	N(2)–C(9)–C(7)	125.2(5)
Sodium ions			
Na(1)–O(12)–Na(2)	94.1(2)		
Na(1)–O(14)–Na(2)	94.2(2)		

[a] e.s.d.s given in parentheses refer to the last significant digit.

Results and Discussion

The phosphonato binuclear complex $Na_2Cu_2L_C$-$OH \cdot 13H_2O$ has been synthesized by reaction of copper(II) acetate with the preformed sodium salt of the ligand H_5L_C in water.

The IR data of Na_5L_C show the $\nu(C{=}N)$ at 1646 cm^{-1} and absorptions attributable to the PO_3^{2-} groups at 1078 and 976 cm^{-1}.

The binuclear complex shows a $\nu(C{=}N)$ at 1645 cm^{-1} and several bands at 1132, 1060, 1028 and 959 cm^{-1} due to the phosphonato groups.

No shifts are detectable for the $\nu(C{=}N)$ band on going from the sodium salt of the ligand to the related binuclear copper complex, but there is a significative splitting of bands associated with the phosphonato groups as a consequence of coordination. The electronic spectrum in nujol mull shows for the binuclear copper complex d–d bands centered at 740 nm which suggest the presence of a non square-planar coordination center. These data do not rule out, for $Na_2Cu_2L_COH \cdot 13H_2O$, more complex structures, as similar IR and UV data have been observed for the tetranuclear $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$ where the copper atoms are square planar and square pyramidal.

For a correct knowledge of the formulation and structure of $Na_2Cu_2L_COH \cdot 13H_2O$, the thermal and magnetic behaviour and the X-ray structure of the crystals grown from water/ethanol were determined. In addition a comparison of these data with those obtained for the basically similar $\{[Cu_2L_A(OH)$-$(H_2O)](dmso)\}_2$ have been carried out.

Thermal Data

Both compounds $Na_2Cu_2L_COH \cdot 13H_2O$ and $Cu_2L_AOH \cdot H_2O$ [2] were tested by thermogravimetric measurements (TG and DTA). The thermogravimetric curves of $Na_2Cu_2L_COH \cdot 13H_2O$ are shown in Fig. 1. The complex presents the endothermic peak due to release of H_2O at 95 °C; the experimental weight loss (28.14%) is in accordance with the calculated value for simultaneous loss of all water molecules (28.64%). At 270 °C there is an exothermal peak relative to a weight loss of 2.04% which can be associated to a molecular rearrangement; this intermediate compound is stable until 395 °C. The decomposition ends at about 550 °C and the final product seems to be $2CuO + Na_2O + P_2O_5$; the experimental total weight loss being 56.5% against a calculated value of 55.59%.

The thermogravimetric degradation of $Cu_2L_AOH \cdot H_2O$ starts at about 260 °C and does not show the release of the water molecule. The first step is due to release of two SO_3 molecules (experimental weight loss 33.18% against a calculated value of 33.94%) immediately followed by decomposition which ends at about 600 °C. The final product seems to be Cu_2O, the experimental total weight loss being 69.12% against a calculated value, for Cu_2O as final product of 69.26%.

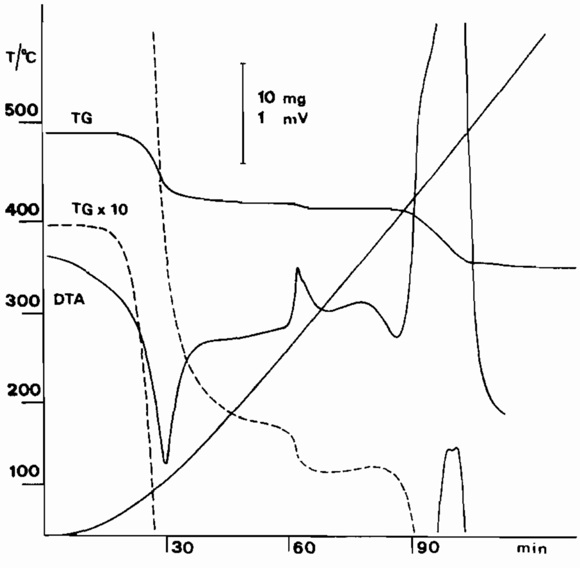

Fig. 1. Simultaneous TG and DTA curves of $Na_2[Cu_2L_COH(H_2O)_2]\cdot 11H_2O$.

X-ray Structure

The compound, whose structure is shown in Fig. 2, is a dinuclear ionic complex and can be formulated as $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$. Six positive charges of two copper and two sodium ions are balanced by five negative charges from L_C^{5-} (one localized on the phenolato oxygen O(7) and four on the terminal phosphonato groups) and by one more charge from the hydroxyl oxygen O(8). The two copper atoms, which are five-coordinated in the square pyramidal arrangement, are bridged through the phenato and the hydroxyl oxygen atoms, the coordination in the base plane being completed for each ion by one nitrogen atom and by one phosphonato oxygen atom. The apical positions are occupied by water molecules. The Cu–O(7) bond distances with the bridging phenato oxygen (mean 1.97 Å) are significantly longer than the corresponding Cu–O(8) distances with the hydroxyl oxygen (mean 1.93 Å), and the observed difference is probably due to the circumstance that the negative charge is obviously localized on the OH^- ion while it is in part delocalized on the C(8)–O(7) bond of the phenato moiety, which is partial double in character (C–O = 1.33 Å). Moreover, the Cu–O(phosphonato) bond distances (both are 1.95 Å) are significantly shorter than the corresponding Cu–O(sulphonato) distances (2.00 and 2.01 Å) in the copper complex $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$ [2], whereas the Cu–N distances are comparable. Cu(1) is displaced by 0.17 Å from the plane defined by the four base atoms. The equation of the mean plane is $0.205\ x - 0.573\ y - 0.793\ z = 0.158$ Å, where x, y, z are orthogonalized atomic coordinates, and deviations of the atoms from the plane are: O(1), 0.042; N(1), −0.059; O(7),

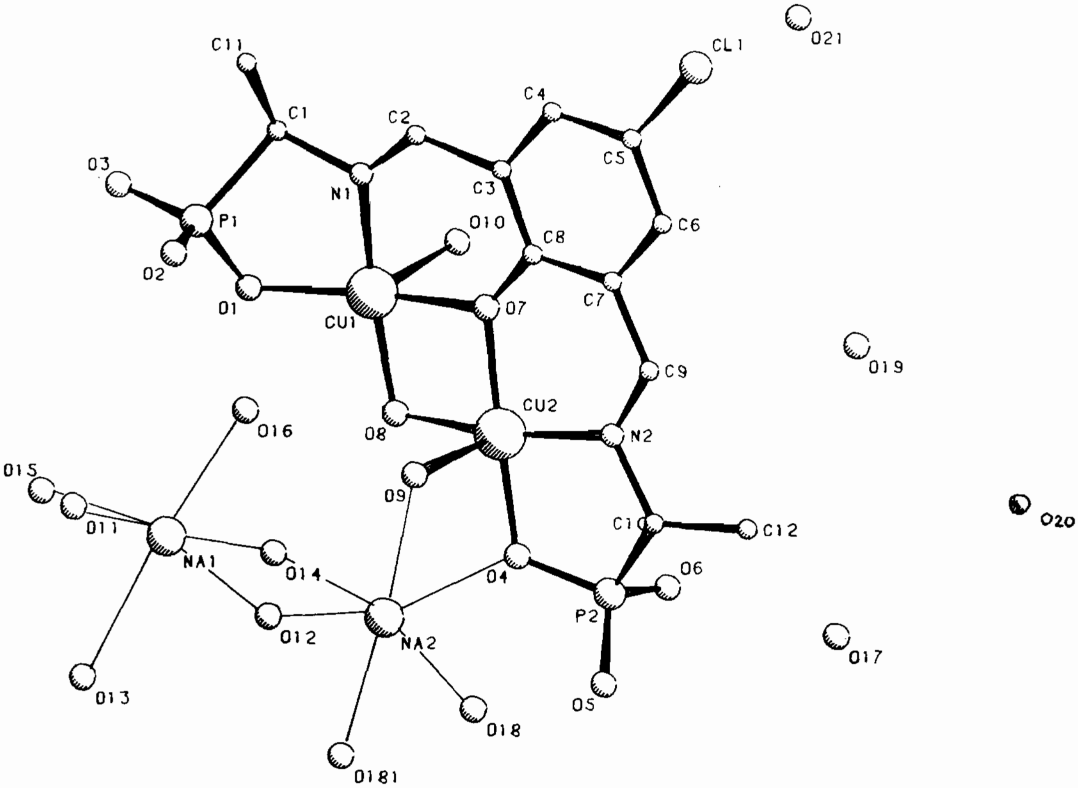

Fig. 2. The crystal structure of $Na_2[Cu_2L_COH(H_2O)_2]\cdot 11H_2O$.

TABLE IV. Proposed Hydrogen Bonds (Å)[a]

O–H...O	O–H	O...O	H...O
O(14)–H(142)...O(1^I)	0.73	2.87	2.18
O(15)–H(152)...O(2^I)	0.65	2.79	2.16
O(16)–H(161)...O(2)	0.71	2.77	2.06
O(18)–H(181)...O(3)	0.71	2.82	2.12
O(11)–H(112)...O(3^I)	0.74	2.81	2.09
O(13)–H(131)...O(3^I)	0.91	2.89	1.99
O(11)–H(111)...O(4)	0.76	2.79	2.04
O(18)–H(182)...O(5)	0.88	2.76	1.93
O(13)–H(132)...O(5^I)	0.84	2.67	1.83
O(17)–H(172)...O(6)	0.92	2.69	1.81
O(12)–H(122)...O(6)	0.82	2.93	2.18
O(16)–H(162)...O(6)	0.72	2.80	2.19
O(8)–H(81)...O(15^I)	0.73	2.78	2.06
O(14)–H(141)...O(8)	0.78	2.84	2.08
O(9)–H(91)...O(16)	0.86	2.75	1.91
O(9)–H(92)...O(17)	0.77	2.87	2.13
O(19)–H(192)...O(10^I)	0.99	2.88	1.90
O(10)–H(101)...O(13^I)	0.78	2.70	1.95
O(15)–H(151)...O(11^I)	0.86	2.80	1.95
O(17)–H(171)...O(3)	0.78	2.96	2.18
O(21)–H(211)...O(17^I)	0.66	2.85	2.19
O(20)–H(201)...O(19)	0.87	2.80	1.96
O(20)–H(202)...O(21)	0.89	2.85	2.06

[a] Donor and hydrogen atoms have the coordinate listed in Table I. Superscript I specifies the $1-x, 1-y, 1-z$ related position of the acceptor oxygen.

0.049; O(8), −0.045 Å. Cu(2) is displaced by 0.085 Å from the base mean plane of equation $0.288\,x - 0.428\,y - 0.857\,z = 2.146$ Å, and deviations of the atoms from the plane are O(4), 0.001; N(2), −0.002; O(7), 0.001; O(8), −0.001 Å. Lines joining Cu(1) and Cu(2) with the apical oxygens O(10) and O(9) form angles of 81.8° and 85.9° with the respective base planes. Water molecules in apical positions are in different bonding situations: O(10) is involved in at least two hydrogen bonds with neighbouring H_2O molecules (Table IV), while O(9) is the apex of the pyramidal arrangement around Cu(2) as well as a corner of the pseudo-octahedral arrangement around Na(2). The Cu...Cu separation (2.964(1) Å) is comparable with values found in $Cu_2(aapen)\cdot H_2O$ [5] and in $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$ [2] (2.96(1) and 2.94(1) Å respectively). The Cu_2O_2 moiety exhibits an arrangement similar to that of $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$. This feature will be discussed in the following paragraph. No unusual feature is present in the pentadentate ligand: C=N double bonds are well localized (mean 1.28 Å). C–P bonds have the expected value (mean 1.83 Å), and P–O bonds with the coordinated oxygens (mean 1.54 Å) are significantly longer than P–O bonds with non-coordinated oxygens (mean 1.51 Å).

Both C(1) and C(10) are asymmetric carbon atoms. The structure shows that both D and L forms of the lateral chains are present with the attached methyl carbon atoms equally distributed in the two possible positions.

Each of the Na^+ cations is surrounded by six oxygen atoms in a rather irregular octahedral arrangement. It is noteworthy that two H_2O molecules, $H_2O(12)$ and $H_2O(14)$ are bridged and that two sites of the octahedral coordination polyhedron around Na(2) are occupied by oxygen atoms shared with Cu(2): O(9) from the above mentioned $H_2O(9)$ molecule and O(4) from a phosphonato group. Angles at Na(1) are in the range 82 to 110°, those at Na(2) are between 74 and 111°. Angles at the bridging oxygens O(12) and O(14) have the same value (94°).

Na–O distances with water oxygens are between 2.38 and 2.50 Å (mean value 2.46 Å) irrespective of whether the oxygens are bridging or not; the Na(2)–O(4) bond with the coordinated phosphonato oxygen appears somewhat longer. The structure is of interest because of an extensive and rather complicated network of hydrogen bonds utilizing the H atoms from the water molecules and from the bridging OH^- group. The pertinent hydrogen bonding parameters are summarized in Table IV.

Magnetic Data

The observed (χ_{obs}) susceptibilities and magnetic effective moments (μ_{eff})* of the complex $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$ are reported in Fig. 3 and Table V. Magnetic parameters are derived from least-squares fitting by using Bleaney–Bowers equation** [11, 12] corrected for the susceptibilities (χ_{param}) of possible paramagnetic impurity [13] and taking into account temperature independent paramagnetism (*TIP*). The equation** also provides the calculated (χ_{calc}) susceptibilities.

The best fitting values $g = 2.10$, $J = -202.5$ cm^{-1} (antiferromagnetic), $TIP = 1.03 \times 10^{-4}$ are in the usual range [2] for complexes of analogous ligands. The amount of paramagnetic impurity is negligible within the experimental errors.

The absolute J value of $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$ is significantly higher than in the complex $Na_2Cu_2L_DOH$ [2], but so far the crystal structure of the latter compound is unknown. More useful is the comparison with the reported results [2] of $Cu_2L_AOH\cdot H_2O$ ($J = -173.7$ cm^{-1}). In this case it is known that the crystal structure of the dimer

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*$\mu_{eff} = 2.828[(\chi_M - \chi_D) \times T]^{1/2}$ BM; $\chi_M = 2 \times \chi_A$; χ_D represents the diamagnetic correction (see ref. 6).

**$\chi_M = \chi_{calc} = (1-\rho)(6 \times 0.1251 g^2)/[T(3 + e^{+2J/kT})] + TIP + \rho\chi_{param}$. The parameters reported in Table V are obtained by minimizing the function $F = \Sigma_N(\chi_{obs} - \chi_{calc})^2$, where N is the number of measurements at different T. The F/N value, taken as a gauge of agreement between calculated and experimental values is small (6×10^{-10}), when compared with actual experimental errors.

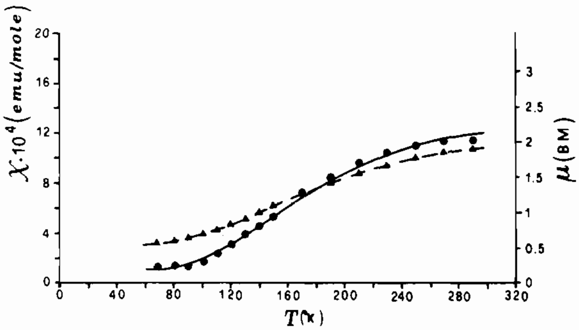

Fig. 3. Observed magnetic susceptibilities (●) and effective magnetic moments (▲) *vs.* temperature for $Na_2[Cu_2L_COH(H_2O)_2]\cdot 11H_2O$. The solid line represents the calculated susceptibilities.

TABLE V. Observed and Calculated Magnetic Susceptibility and Effective Magnetic Moment *versus* Temperature for $Na_2[Cu_2L_C(OH)(H_2O)_2]\cdot 11H_2O$

T	$\chi_{obs} \times 10^{-4}$	$\chi_{calc} \times 10^{-4}$	μ_{eff}
68	1.38	1.13	0.56
80	1.38	1.32	0.61
90	1.42	1.60	0.65
100	1.78	2.00	0.71
110	2.41	2.52	0.78
120	3.08	3.14	0.85
130	3.95	3.82	0.93
140	4.62	4.56	1.01
150	5.41	5.32	1.09
170	7.31	6.81	1.26
190	8.38	8.17	1.40
210	9.68	9.34	1.54
230	10.31	10.28	1.65
250	10.98	11.03	1.76
270	11.26	11.58	1.84
290	11.50	11.98	1.92

$\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$ contains at least the Cu_2L_AOH moiety. In turn, the side chain length of the sulphonic H_3L_A ligand is similar to that of H_5L_C, since both ligands derive from α-aminoacids.

Actually the Cu...Cu distance (2.964(1) Å) for $Na_2[Cu_2L_COH(H_2O)_2]\cdot 11H_2O$ is significantly larger than that previously reported for $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$ (2.940(3) Å) [2], consistent (since in both compounds the Cu_2O_2 moiety is planar) with larger Cu–O–Cu angles (average value 99.0°), compared with 97.8° in $\{[Cu_2L_A(OH)(H_2O)](dmso)\}_2$.

This trend is in tune with those previously reported [14, 15]. For a series of hydroxo-bridged copper(II) dimers a monotonic decrease of the value of J as the value of the Cu–O–Cu angle increases was found. However a larger series of homogeneous data of analogous compounds is needed in order to assess a definite trend in magnetic behaviour.

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