

were determined. Moreover, interatomic distances in the Ta₆Cl₁₈ unit are in good agreement with the corresponding distances reported for such a unit (Brnićević, Ružić-Toroš, Kojić-Prodić, 1985; Slougui *et al.*, 1989).

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Lewis-Base Adducts of Group 11 Metal(I) Compounds. 60. Binuclear Adducts of Copper(I) Halides with 2-Hindered Pyridine Bases

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Abstract. (I): Di- μ -bromo-bis[bis(2-bromopyridine)-copper(I)], [Cu₂Br₂(C₅H₄BrN)₄], $M_r = 918.9$, triclinic, $P\bar{1}$, $a = 10.224(4)$, $b = 8.935(2)$, $c = 7.892(2)$ Å, $\alpha = 68.84(2)^\circ$, $\beta = 71.96(3)^\circ$, $\gamma = 83.23(3)^\circ$, $V = 639(1)$ Å³, $Z = 2$, $D_x = 2.39$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 109$ cm⁻¹, $F(000) = 864$, $T = 293$ K, final $R = 0.052$. (II): Di- μ -chloro-bis[bis(2-benzylpyridine)copper(I)], [Cu₂Cl₂(C₁₂H₁₁N)₄], $M_r = 874.9$, triclinic, $P\bar{1}$, $a = 16.441(5)$, $b = 9.183(5)$, $c = 7.661(2)$ Å, $\alpha = 76.87(4)^\circ$, $\beta = 81.65(3)^\circ$, $\gamma = 73.17(4)^\circ$, $V = 1074(1)$ Å³, $Z = 2$, $D_x = 1.35$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 8.1$ cm⁻¹, $F(000) = 452$, $T = 293$ K, final $R = 0.047$.

Experimental. (I): Prism, dark red–brown, crystal size 0.44 × 0.35 × 0.20 mm, scintillation detector. Diffraction measurement method: $2\theta/\theta$, diffraction temperature 293 K. Absorption correction type: analytical. T_{\min} , T_{\max} not recorded. $\theta_{\min} = 2.09^\circ$, $\theta_{\max} = 27.47^\circ$; h 0→13, k -11→11, l -9→10. Six standard reflections, measured every 100 reflections, intensity variation 0%. Criterion for observed reflections: $I > 3\sigma(I)$. Full-matrix least-squares refinement, 1909 reflections 'observed' out of 2934 independent measured; number of parameters in least-squares refinement 145, $wR(\text{all reflections}) = 0.061$,

$wR(\text{observed reflections}) = 0.059$, $S(\text{all reflections}) = 2.29$, $S(\text{observed reflections}) = 2.77$, weights based on measured σ 's; $(\Delta/\sigma)_{\max} = 0.088$, $(\Delta/\sigma)_{\text{mean}} = 0.004$, $\Delta\rho_{\max} = 0.966$, $\Delta\rho_{\min} = -0.946$ e Å⁻³, no correction for secondary extinction.

(II): Plate, colourless, crystal size 0.5 × 0.2 × 0.03 mm, scintillation counter. Diffraction measurement method: $2\theta/\theta$, diffraction temperature 293 K. Absorption correction type: Gaussian. $A_{\min}^* = 1.03$, $A_{\max}^* = 1.17$. $\theta_{\min} = 1.30^\circ$, $\theta_{\max} = 24.99^\circ$; h 0→19, k -10→10, l -8→9. Eight standard reflections, measured every 100 reflections, intensity variation 0%. Criterion for observed reflections: $I > 3\sigma(I)$. Full-matrix least-squares refinement, 2189 reflections 'observed' out of 3778 independent measured; number of parameters in least-squares refinement 254, $R(\text{all reflections}) = 0.098$, $wR(\text{all reflections}) = 0.057$, $wR(\text{observed reflections}) = 0.050$, $S(\text{all reflections}) = 1.26$, $S(\text{observed reflections}) = 1.48$, weights based on measured σ 's; $(\Delta/\sigma)_{\max} = 0.101$, $(\Delta/\sigma)_{\text{mean}} = 0.012$, $\Delta\rho_{\max} = 0.370$, $\Delta\rho_{\min} = -0.368$ e Å⁻³, Gaussian extinction correction (Zachariasen, 1963), secondary-extinction coefficient = 0.131.

Data collection: Enraf–Nonius CAD-4 software. All calculations and diagrams were performed with the XTAL3.0 package (Hall & Stewart, 1990), as was the

Table 1. Atomic positional parameters and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

Compound (I)	x	y	z	U _{eq}
Br1	0.0774(1)	0.9321(1)	0.7008(1)	0.045(1)
Br12	0.2888(1)	0.5788(1)	0.5870(2)	0.061(1)
Br22	0.2691(1)	1.1045(1)	-0.1067(1)	0.055(1)
Cu1	0.1441(1)	0.9325(1)	0.3674(2)	0.046(1)
N11	0.1529(8)	0.7204(8)	0.320(1)	0.035(7)
C12	0.1961(9)	0.579(1)	0.413(1)	0.037(9)
C13	0.181(1)	0.437(1)	0.394(1)	0.05(1)
C14	0.118(1)	0.441(1)	0.260(2)	0.05(1)
C15	0.073(1)	0.585(1)	0.156(1)	0.05(1)
C16	0.090(1)	0.720(1)	0.190(1)	0.041(9)
N21	0.3170(8)	1.0772(8)	0.228(1)	0.040(8)
C22	0.362(1)	1.152(1)	0.042(1)	0.05(1)
C23	0.471(1)	1.255(1)	-0.048(2)	0.07(1)
C24	0.536(1)	1.285(1)	0.061(2)	0.08(2)
C25	0.492(1)	1.209(1)	0.257(2)	0.07(1)
C26	0.383(1)	1.105(1)	0.335(2)	0.05(1)
H13	0.2142	0.3391	0.4685	0.06206
H14	0.1059	0.3431	0.2438	0.06586
H15	0.0317	0.5908	0.0610	0.07346
H16	0.0563	0.8206	0.1194	0.05446
H23	0.5015	1.3035	-0.1807	0.07472
H24	0.6104	1.3593	0.0060	0.09372
H25	0.5382	1.2259	0.3363	0.09625
H26	0.3528	1.0526	0.4693	0.06839
Compound (II)	x	y	z	U _{eq}
Cu1	0.08803(4)	1.02385(8)	0.4594(1)	0.0532(7)
Cl1	0.03152(8)	0.8583(1)	0.7276(2)	0.047(1)
N1	0.0998(3)	1.2004(4)	0.5599(6)	0.041(4)
N2	0.1673(2)	0.8678(4)	0.3225(5)	0.039(4)
C111	0.1223(3)	1.3257(6)	0.4587(8)	0.047(5)
C112	0.1127(4)	1.4577(6)	0.528(1)	0.066(6)
C113	0.0820(4)	1.4598(7)	0.704(1)	0.073(7)
C114	0.0607(4)	1.3319(7)	0.8094(9)	0.066(6)
C115	0.0706(4)	1.2052(6)	0.7331(8)	0.052(5)
C116	0.1582(4)	1.3140(7)	0.2698(9)	0.065(6)
C121	0.2499(4)	1.2175(7)	0.256(1)	0.069(7)
C122	0.3088(5)	1.2226(8)	0.363(1)	0.087(8)
C123	0.3933(6)	1.134(1)	0.350(2)	0.12(1)
C124	0.4171(7)	1.043(1)	0.223(2)	0.15(2)
C125	0.3618(9)	1.032(1)	0.120(2)	0.14(1)
C126	0.2771(6)	1.122(1)	0.132(1)	0.095(9)
C211	0.2412(3)	0.7751(6)	0.3822(7)	0.040(5)
C212	0.2937(3)	0.6695(7)	0.2850(7)	0.053(5)
C213	0.2716(4)	0.6571(7)	0.1251(8)	0.066(6)
C214	0.1957(4)	0.7497(7)	0.0643(7)	0.062(6)
C215	0.1456(3)	0.8541(6)	0.1657(7)	0.050(5)
C216	0.2627(3)	0.7962(6)	0.5580(7)	0.052(5)
C221	0.3316(3)	0.6650(6)	0.6455(7)	0.044(5)
C222	0.4069(4)	0.6882(7)	0.6685(9)	0.064(6)
C223	0.4707(4)	0.570(1)	0.753(1)	0.085(8)
C224	0.4589(5)	0.4266(9)	0.811(1)	0.083(8)
C225	0.3844(5)	0.3994(7)	0.7913(9)	0.073(7)
C226	0.3185(4)	0.5198(7)	0.7094(8)	0.058(6)
H112	0.1287	1.5476	0.4490	0.10626
H113	0.0763	1.5521	0.7483	0.12247
H114	0.0386	1.3323	0.9368	0.11209
H115	0.0559	1.1137	0.8078	0.08878
H116	0.1239	1.2690	0.2162	0.11601
H117	0.1546	1.4167	0.1986	0.11601
H122	0.2907	1.2892	0.4519	0.14122
H123	0.4363	1.1346	0.4263	0.17693
H124	0.4731	0.9832	0.2000	0.18605
H125	0.3783	0.9617	0.0330	0.19643
H126	0.2346	1.1177	0.0541	0.14489
H212	0.3472	0.6040	0.3312	0.07941
H213	0.3092	0.5822	0.0575	0.09739
H214	0.1777	0.7417	-0.0481	0.09967
H215	0.0916	0.9216	0.1236	0.08131

Table 1 (cont.)

	x	y	z	U _{eq}
H216	0.2806	0.8898	0.5379	0.09891
H217	0.2124	0.8080	0.6407	0.09891
H222	0.4159	0.7916	0.6241	0.10081
H223	0.5240	0.5894	0.7701	0.12817
H224	0.5050	0.3428	0.8678	0.11715
H225	0.3775	0.2966	0.8314	0.10968
H226	0.2642	0.5008	0.6981	0.09144

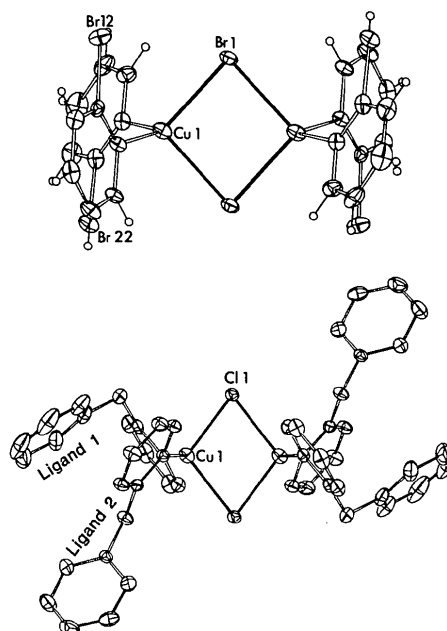


Fig. 1. Molecules of the two complexes projected normal to their CuX₂Cu planes; each dimer is centrosymmetric. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms when shown have arbitrary radii of 0.1 Å.

generation of the Crystallographic Information File used for the submission of this paper. Atomic coordinates are listed in Table 1.* Fig. 1 shows molecules of the two complexes.

Related literature. 1:2 adducts of copper(I) halides, CuX (X = Cl, Br, I) with monodentate nitrogen ligands, L, commonly adopt two forms: a binuclear μ , μ' -dihalo-bridged structure $L_2CuX_2CuL_2$, containing four-coordinated copper(I), and mononuclear L_2CuX containing three-coordinate copper. The latter is obtained by the recrystallization of the copper(I) halide from solution in pyridine bases hindered with methyl groups in both 2- and 6-positions, such as 2,6-dimethylpyridine (Healy, Pakawatchai & White, 1983; Dyason, Healy,

* Lists of structure factors, anisotropic thermal parameters and complete lists of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53794 (27 pp.). Copies may be obtained through the Technical Editor, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

Compound (I)		Compound (II)	
Br1—Cu1	2.504(2)	Cu1—Cl1	2.498(2)
Br1—Cu1'	2.553(2)	Cu1—N1	2.013(5)
Cu1—N11	2.048(8)	Cu1—N2	2.014(4)
Cu1—N21	2.077(8)	Cu1—Cu1'	3.008(1)
		Cu1—Cl1'	2.443(2)
Cu1—Br1—Cu1'	85.02(6)	Cu1—Cl1—Cu1'	74.98(6)
Br1—Cu1—N11	119.6(2)	Cl1—Cu1—N1	103.1(1)
Br1—Cu1—N21	104.5(3)	Cl1—Cu1—N2	103.2(1)
Br1—Cu1—Br1'	94.98(6)	Cl1—Cu1—Cl1'	105.03(6)
N11—Cu1—N21	116.8(3)	N1—Cu1—N2	135.0(2)
N11—Cu1—Br1'	104.7(2)	N1—Cu1—Cl1'	104.0(1)
N21—Cu1—Br1'	114.5(2)	N2—Cu1—Cl2'	103.5(1)

Pakawatchai, Patrick & White, 1985), while binuclear species may be obtained by direct recrystallization of the copper(I) halide from solution in a pyridine base with carbon substituent in the 2-position only, as with 2-methylpyridine or quinoline (Healy, Pakawatchai & White, 1983; Dyason, Engelhardt, Healy, Pakawatchai & White, 1985), or with a 1:2 stoichiometry from an appropriate supporting solvent. In exploring further the role

and volume of the 2-substituent in controlling stoichiometry and structure in the adducts, we have determined the structures of these further adducts with 2-substituted pyridine ligands, the substituents being benzyl and bromo moieties, and record the structure determinations hereunder, with copper(I) chloride and bromide respectively, as 1:2 binuclear dimers. By comparison with selected studies in the above references, the $N_2CuX_2CuN_2$ molecular core geometries (Table 2) are unremarkable.

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Structure of $[LFe(\mu\text{-MoO}_4)_3FeL]\cdot CH_2Cl_2\cdot H_2O$ ($L = 1,4,7\text{-Trimethyl-1,4,7-triazacyclononane}$)

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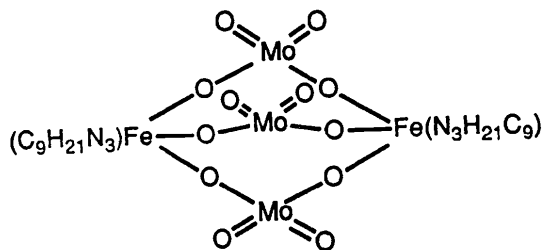
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Abstract. Tri- μ -molybdate(2-)-bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)iron(III)]-dichloromethane-water (1/1/1), $[Fe_2(MoO_4)_3(C_9H_{21}N_3)_2]\cdot CH_2Cl_2\cdot H_2O$, $M_r = 1037.0$, orthorhombic, *Pbca*, $a = 15.239$ (2), $b = 16.376$ (3), $c = 28.964$ (4) Å, $V = 7227.9$ (17) Å³, $D_x = 1.91$ g cm⁻³, $Z = 8$, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 19.8$ cm⁻¹, $F(000) = 4144$, $T = 293$ K, $R = 0.047$, $wR = 0.051$ for 2457 observed reflections. The structure consists of a tri- μ -molybdate-diiron(III) molecular cluster, similar to that of $[LFe(CrO_4)_3FeL]\cdot H_2O$ ($L = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$) [Chaudhuri, Winter, Wieghardt, Gehring, Haase, Nuber & Weiss (1988). *Inorg. Chem.* **27**, 1564–1569]. The synthesis from acetonitrile affords a convenient preparation of crystalline complex and avoids the use of perchlorate salts. The complex provides an unusual example of an early-transition-metal polyoxoanion which is neutral, rather than

anionic as is the case with the vast majority of polyoxometalate species [Pope (1983). *Heteropoly and Isopoly Oxometalates*. Berlin: Springer-Verlag].

Experimental. The title compound (I) was obtained from the reaction of $(C_9H_{21}N_3)FeCl_3$ (Chaudhuri, Winter, Wieghardt, Gehring, Haase, Nuber & Weiss, 1988) and $[(C_4H_9)_4N]_2[Mo_2O_7]$ (Day, Fredrich, Klemperer & Shum, 1977) (1:2.5) in refluxing acetonitrile, followed by recrystallization from dichloromethane/methanol (2:1).



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