is bonded to the Cu^{II} atom only through O(4), with the Cu—O(4) bond length [2·374 (4) Å] significantly shorter than that of Cu—O(2).

The molecules of the complex are held together by a system of intermolecular hydrogen bonds formed between O atoms O(3), O(5) and O(6), respectively, and the secondary [H(8)] and primary [H(13) and H(14)] amine H atoms of neighboring molecules [2·15 (6), 2·25 (6), 2·19 (7) and 2·35 (7) Å for O(5)···H(8), O(6)···H(8), O(5)···H(13) and O(3)···H(14), respectively].

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Structure of *trans*-Bis(1,4-butanedione dioximato)bis(triphenylarsine)copper(II), $[Cu(Hdmg)_2(Ph_3As)_2]$

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Abstract. $C_{44}H_{44}As_2CuN_4O_4$, M_r = 906·24, monoclinic, $P2_1/c$, a = 8·972 (2), b = 15·730 (3), c = 15·074 (3) Å, β = 105·95 (2)°, Z = 2, V = 2045·6 (9) Å^3, D_m = 1·471, D_x = 1·471 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 29·163 cm^{-1}, F(000) = 926, room temperature, R = 0·053, wR = 0·062 for 1869 reflections with $I \geq 3\sigma(I)$. The structure consists of isolated centrosymmetric $[Cu(Hdmg)_2(Ph_3As)_2]$ molecules (Hdmg = $C_4H_7N_2O_2$). Copper is hexacoordinated with dioximate ligands in the equatorial plane and the axial Ph_3As ligands [Cu—As = 3·044 (1) Å].

Introduction. In the course of our study of the stabilization of Cu^{II} complexes with reducing ligands, $[Cu(Hdmg)_2(Ph_3P)]$ has been prepared (Ondrejovič, Máriássy & Koman, 1989). The related complexes with copper/phosphine or copper/arsine ratios of 1/2 are unusual; addition of a second Ph_3P or Ph_3As ligand to pentacoordinate β-diketonate copper(II) complexes (Zelonka & Baird, 1972) invariably leads to the reduction of Cu^{II} to Cu^{I}. The title complex is therefore a copper dioximate arsine of novel type (Ondrejovič, Máriássy & Koman, 1989). Because of this and also since there is a paucity of known structures of copper(II)–R_3E (E = P,As,Sb) complexes [only dimeric copper carboxylates with Ph_3P were structurally characterized (McCrindle, Ferguson, McAlees & Roberts, 1981; Koman, Valigura & Ondrejovič, 1988)] a structure determination of the title complex was undertaken.

Experimental. Dark-brown prism-shaped crystals (Máriássy, 1988), 0·30 × 0·15 × 0·20 mm; density measured by flotation. Syntex $P2_1$ diffractometer, 15 reflections with 8·14 ≤ θ ≤ 15·10° for determining lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for 0 ≤ 2θ ≤ 100°. h 0–9, k 0–16, l −15–15. Two reflections every 98 measurements decreased in intensity by 15% during the course of the experiment, 1869 independent reflections with $I \geq 3\sigma(I)$, 237 unobserved reflections. Cu- and As-atom positions from Patterson function, other non-H atoms from Fourier syntheses. Position of H(1) from difference synthesis; those of other H atoms were calculated. Anisotropic full-matrix refinement for non H-atoms based on F. R = 0·053, wR = 0·062, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ (k = 1·0000, g = 0·01633); $(\Delta/\sigma)_{max}$ = 0·8 in final least-squares cycle; $|\Delta\rho| \leq$ 0·9 e Å^{-3}. Calculations performed with *SHELX76*

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\times 10^4$) *for non-*H *atoms, with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cu1	0·0	0·0	0·0	5·21 (4)
As1	0·0339 (1)	0·0442 (1)	−0·1901 (1)	3·10 (3)
N1	−0·0031 (6)	0·1213 (3)	0·0223 (3)	4·02 (15)
N2	0·2206 (5)	0·0178 (3)	0·0425 (3)	3·82 (14)
O1	−0·1342 (5)	0·1659 (3)	0·0088 (3)	5·30 (14)
O2	0·3285 (5)	−0·0430 (3)	0·0475 (4)	5·16 (15)
C1	0·1340 (7)	0·1564 (4)	0·0520 (4)	3·94 (17)
C3	0·1527 (8)	0·2498 (4)	0·0756 (4)	5·99 (21)
C2	0·2623 (6)	0·0959 (4)	0·0611 (4)	4·02 (20)
C4	0·4276 (8)	0·1219 (6)	0·0921 (6)	6·81 (27)
C11	0·1714 (6)	0·1426 (3)	0·8173 (3)	3·57 (16)
C12	0·1194 (6)	0·2219 (4)	0·8368 (4)	3·99 (18)
C13	0·2188 (7)	0·2915 (4)	0·8492 (4)	4·65 (20)
C14	0·3707 (7)	0·2813 (4)	0·8441 (5)	5·09 (21)
C15	0·4202 (7)	0·2037 (4)	0·8269 (5)	5·02 (21)
C16	0·3195 (7)	0·1329 (4)	0·8154 (4)	4·21 (19)
C21	0·1180 (6)	0·9712 (4)	0·7291 (3)	3·15 (16)
C22	0·1156 (7)	0·9943 (4)	0·6407 (4)	4·34 (19)
C23	0·1695 (8)	0·9387 (4)	0·5853 (5)	4·80 (20)
C24	0·2261 (7)	0·8600 (4)	0·6191 (5)	5·03 (21)
C25	0·2319 (7)	0·8380 (4)	0·7080 (4)	4·40 (15)
C26	0·1753 (6)	0·8926 (3)	0·7639 (4)	3·20 (15)
C31	0·8415 (6)	0·0795 (3)	0·7201 (4)	3·16 (15)
C32	0·8240 (6)	0·1511 (4)	0·6651 (4)	3·92 (18)
C33	0·6829 (7)	0·1698 (4)	0·6004 (4)	4·52 (18)
C34	0·5583 (8)	0·1160 (5)	0·5959 (5)	5·81 (23)
C35	0·5727 (8)	0·0448 (5)	0·6538 (7)	6·69 (29)
C36	0·7141 (8)	0·0282 (4)	0·7141 (5)	5·08 (22)

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu1—As1	3·044 (1)	C1—C2	1·473 (7)
Cu1—N1	1·938 (4)	C1—C3	1·510 (7)
Cu1—N2	1·925 (4)	C2—C4	1·484 (8)
N1—O1	1·337 (5)	As1—C11	1·962 (4)
N2—O2	1·350 (5)	As1—C21	1·969 (4)
N1—C1	1·309 (6)	As1—C31	1·959 (4)
N2—C2	1·292 (6)		

N1—Cu1—N2	97·9 (2)	C21—As1—C31	98·9 (2)
N1—Cu1—As1	87·0 (1)	Cu1—N1—O1	123·0 (3)
N2—Cu1—As1	94·6 (1)	Cu1—N2—O2	124·9 (3)
Cu1—As1—C11	110·5 (1)	C1—N1—O1	122·3 (4)
Cu1—As1—C21	127·1 (1)	C2—N2—O2	122·2 (4)
Cu1—As1—C31	114·7 (1)	Cu1—N1—C1	114·6 (3)
C11—As1—C21	98·9 (2)	Cu1—N2—C2	112·2 (4)
C11—As1—C31	103·6 (2)		

(Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The final coordinates of non-H atoms are listed in Table 1* and selected interatomic distances and angles in Table 2. The molecular structure of $[Cu(Hdmg)_2(Ph_3As)_2]$ and the atomic numbering are shown in Fig. 1.

The crystal structure is built of tetragonal-bipyramidal centrosymmetric molecules, held together by van der Waals interactions. The equatorial plane is formed by the four N atoms of the planar dioximate ligands. The mean Cu—N bond length of 1·932 (4) Å is significantly shorter than values for other copper dioximate complexes: *e.g.* hexacoordinate copper 1·950 (1) Å in $[Cu(Hhd)_2(tu)_2]$ (Koman, Máriássy & Ondrejovič, 1990*a*), pentacoordinate copper 1·952 (4) Å in $[Cu_2(Hdmg)_2]$ (Vaciago & Zambonelli, 1970), 1·955 (1) Å in $[Cu(Hdmg)_2(Him)]$ (Morehouse, Polychronopoulou & Williams, 1980), 1·944 (14) Å in $[Cu(Hdpg)_2(H_2O)]$ (Boualam & Gleizes, 1983) and 1·952 (3) Å in $[Cu(Hdmg)_2(tu)]$ (Koman, Máriássy & Ondrejovič, 1990*b*) (Hhd = 3,4-hexanedionedioximate, tu = thiourea, Him = imidazole, Hdpg = benzyldione dioximate).

The O—H···O hydrogen bonds joining the two dioximate ligands are nearly symmetrical [O—H distances 1·29 (7) and 1·36 (7) Å]. The axial Cu—As distance of 3·044 (1) Å is much longer than values in tetrahedral Cu^{II} complexes [2·33 (1) and 2·43 (1) Å; Mazhar-U1-Haque, Ahmed, Tayim & Horne, 1987], but compares well with the Cu—S distance of 2·940 (1) Å in $[Cu(Hhd)_2(tu)_2]$ (Koman, Máriássy & Ondrejovič, 1990*a*). The arsine ligands are slightly displaced from ideal axial positions, the angle between the Cu—As bond and the normal to the equatorial plane being 5·1°. Bond lengths and angles of triphenylarsine in the complex are similar to those reported for free and coordinated triphenylarsine (Sobolev, Belskij, Černikova & Achmadulinova, 1983; Mazhar-U1-Haque, Ahmed, Tayim & Horne, 1987).

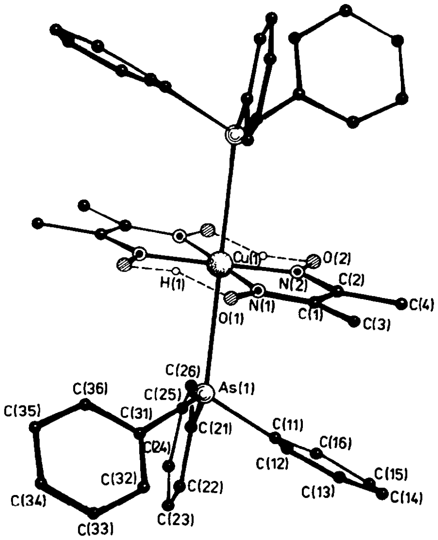

Fig. 1. The molecular structure of $Cu(Hdmg)_2(Ph_3As)_2$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53858 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The present structure represents a new structural type of copper arsine and copper dioximate complex.

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Structural Investigations of Nickel(II) Complexes. IX. Structure of Tetrakis(imidazole)bis(isothiocyanato)nickel(II)

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Abstract. $[Ni(NCS)_2(C_3H_4N_2)_4]$, $M_r = 447{\cdot}18$, orthorhombic, $Pbca$, $a = 15{\cdot}415\,(6)$, $b = 16{\cdot}422\,(5)$, $c = 15{\cdot}535\,(4)$ Å, $V = 3932{\cdot}6\,(2)$ Å^3, $Z = 8$, $D_m = 1{\cdot}50$, $D_x = 1{\cdot}510$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 34{\cdot}06$ cm^{-1}, $F(000) = 1840$, room temperature, $R = 0{\cdot}0486$, $wR = 0{\cdot}0505$ for 1867 reflections with $I \geq 3\sigma(I)$. The structure consists of isolated molecules of $[Ni(NCS)_2(Him)_4]$ (Him = imidazole), which contains a distorted octahedral NiN_6 chromophore. The NCS ligands are *trans* and four N(imidazole) atoms define an equatorial plane. The mean Ni—N(Him) distance (R_e) is 2·113 (4) and the mean Ni—N(Him) distance (R_a) is 2·080 (3) Å.

Introduction. From the spectral and magnetic data it has been concluded that stereochemical and other properties of Ni^{II} pyridine complexes are influenced by the nature and position of substituents on the pyridine ligands (Jamnický & Jóna, 1984). Furthermore, it was shown by Koman, Jóna & Ďurčanská (1986) that the stereochemistry of $[Ni(NCS)_2L_4]$ complexes, where L is a piperidine derivative, depends on the position of methyl substituents in the piperidine ring. When L = piperidine itself, Ni^{II} displays a pseudooctahedral configuration, while the complexes with 3- and 4-methylpiperidine contain pentacoordinated Ni and those with 2-methyl and 2,6-dimethylpiperidine are square planar (Koman, Ďurčanská, Handlovič & Gažo, 1985).

The present paper deals with the structure of tetrakis(imidazole)bis(isothiocyanato)nickel(II). It was expected that exchange of pyridine or piperidine (six-membered-ring heterocyclic ligands) by imidazole which has a five-membered ring might be accompanied by a change in Ni—N bond lengths and by a different type of axial distortion of the metal coordination.

Experimental. Blue prism-shaped crystals, 0·40 × 0·20 × 0·15 mm; density measured by flotation. Syntex $P2_1$ diffractometer, 15 reflections with $5{\cdot}37 \leq \theta \leq 12{\cdot}85°$ for determining lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 100°$; h, k, l range h 0 to 16, k 0 to 17, l 0 to 16. Two standard reflections re-estimated after every 98 measurements, decreased in intensity by 15% during the course of the experiment. 1867 independent reflections with $I \geq 3\sigma(I)$ (511 unobserved reflections), 308 refined parameters. Ni-atom position from Patterson function, other non-H atoms from Fourier syntheses. H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms (H atoms isotropic refinement) based on F. $R = 0{\cdot}0486$, $wR = 0{\cdot}0505$. $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$, $k = 2{\cdot}5456$, $g = 0{\cdot}000886$, $|\Delta\rho| \leq 0{\cdot}7$ e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}40$ in final least-squares cycle. Calculations performed with *SHELX76* program system (Sheldrick,

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