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Structures of Copper(II)–Imidazole Complexes: Diethylenetriamine(imidazole)copper(II) Perchlorate (1) and Diethylenetriamine(1-ethylimidazole)copper(II) Perchlorate (2)

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Abstract. (1): $[Cu(C_3H_4N_2)(C_4H_{13}N_3)](ClO_4)_2$, $M_r = 433{\cdot}69$, orthorhombic, $Pnma$, $a = 14{\cdot}043\ (2)$, $b = 9{\cdot}322\ (2)$, $c = 12{\cdot}347\ (2)$ Å, $U = 1616{\cdot}3\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}782$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}78$ mm^{-1}, $F(000) = 884$, $T = 293$ K, final $R = 0{\cdot}061$ for 1596 observed reflections. (2): $[Cu(C_4H_{13}N_3)(C_5H_8N_2)](ClO_4)_2$, $M_r = 461{\cdot}75$, monoclinic, $P2_1/c$, $a = 8{\cdot}326\ (2)$, $b = 14{\cdot}600\ (3)$, $c = 15{\cdot}055\ (3)$ Å, $\beta = 94{\cdot}88\ (2)°$, $U = 1823{\cdot}4\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}682$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}58$ mm^{-1}, $F(000) = 948$, $T = 293$ K, final $R = 0{\cdot}074$ for 2859 observed reflections. The structures of both complexes are similar to each other. The coordination geometry around the Cu atom in each complex is octahedral, with the four N atoms from the diethylenetriamine and imidazole ligands occupying the equatorial sites and two O atoms of the perchlorate anions semicoordinated at the apical sites. Bond lengths and angles in the diethylenetriamine ligand and between the Cu atom and the ligand are normal.

Introduction. It is well known that the imidazole of the histidine residue plays an important role in metalloproteins. In this connection, the chemistry of imidazolate-bridged bimetallic complexes has been widely investigated. Recently, it has been found that a copper(II)–imidazolate complex of the type $[Cu(dien)(Im)]ClO_4$* (3) is afforded from the treatment of a corresponding copper(II)–imidazole complex, $[Cu(dien)(ImH)(ClO_4)_2]$ (1), with a strong base, and X-ray crystallography has revealed that the structure of (3) is of a polynuclear type with trigonal-bipyramidal Cu$^{\text{II}}$ atoms (Sato, Nagae, Ohmae, Nakaya, Miki & Kasai, 1986). We describe here the structures of the starting material of the above-mentioned reaction, (1), and of its 1-ethylimidazole analogue, $[Cu(dien)(ImEt)(ClO_4)_2]$ (2), where the pyrrole H atom of the imidazole in (1) is replaced by an ethyl group.

Experimental. Both complexes were prepared by the addition of equimolar amounts of cupric perchlorate, dien and imidazole ligand in methanol–acetonitrile solutions. Crystals used were obtained from methanol solutions containing about 10% water (by volume). Systematic absences of (1), $0kl$ $k + l$ odd and $hk0$ h odd, indicated space group $Pn2_1a$ or $Pnma$, while that of (2) was uniquely determined as $P2_1/c$.

Purple, prismatic crystals with approximate dimensions of $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}40$ mm for (1) and $0{\cdot}15 \times 0{\cdot}25 \times 0{\cdot}35$ mm for (2). Rigaku automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters by least-squares refinement, θ–2θ scan technique, scan range $\Delta(2\theta) = (1{\cdot}8 + 0{\cdot}70\tan\theta)°$, scan speed 4° min^{-1} in 2θ, background intensity measured 7·5 s at both ends of a scan, $2\theta_{\max} = 54°$, index range $h = 0$ to 17, $k = 0$ to 11, $l = 0$ to 15 for (1) and $h = -10$ to 10, $k = 0$ to 18, $l = 0$ to 19 for (2). Three standard reflections [600, 060, and 0,10,0 for (1), 400, 006, and 080 for (2)] measured

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* Abbreviations used: dien = diethylenetriamine, ImH = imidazole, ImEt = 1-ethylimidazole and Im = imidazolate.

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every 60 reflections varied less than 1%, absorption corrections omitted, Lorentz–polarization correction made, total numbers of measured and independent reflections 4690 and 1869 for (1), 4430 and 3981 for (2), $R_{\rm int} = 0{\cdot}023$ and 0·016 for (1) and (2), respectively.

Heavy-atom method; Cu atom from Patterson map, remaining non-H atoms from a subsequent Fourier map. Block-diagonal least-squares refinement on F using *HBLSV* (Ashida, 1979), anisotropic thermal parameters for non-H atoms, all the H atoms except for those of the ethyl group of (2) from a difference Fourier map included in the final stages of refinement. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Because of the ambiguity in the space group of (1), the structure was refined in both *Pnma* and $Pn2_1a$. Despite the higher number of parameters in $Pn2_1a$, the R factors for the two structures are approximately the same. The molecular geometry after refinement in $Pn2_1a$ was much poorer than that in *Pnma*; for example, the N(11)–C(12) bond length in the dien ligand was 1·473 Å for the centrosymmetric structure, whereas in the noncentrosymmetric structure two corresponding chemically equivalent bond lengths were 1·459 and 1·597 Å. The space group was therefore taken to be *Pnma* in the further refinement, where the imidazole group has, however, a disordered structure because the crystallographic mirror plane bisects the imidazole plane.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters of non-*H *atoms with e.s.d.'s*

	x	y	z	$B_{\rm eq}$*(Å^2)
Complex (1)				
Cu	0·21635 (5)	0·25	0·10004 (6)	3·7
N(1)	0·3461 (4)	0·25	0·0394 (4)	4·3
C(2)	0·3796 (7)	0·3234 (12)	−0·0413 (9)	6·1
N(3)	0·4691 (5)	0·2852 (21)	−0·0639 (6)	6·6
C(4)	0·4918 (7)	0·1786 (15)	0·0027 (12)	8·0
C(5)	0·4182 (7)	0·1534 (14)	0·0670 (10)	7·7
N(11)	0·2047 (3)	0·0364 (5)	0·1144 (4)	4·7
C(12)	0·1063 (4)	−0·0040 (6)	0·1424 (5)	6·3
C(13)	0·0547 (4)	0·1158 (6)	0·1875 (7)	7·4
N(14)	0·0790 (4)	0·25	0·1465 (5)	4·9
Cl(1)	0·27677 (11)	0·25	0·39236 (11)	4·2
O(11)	0·3034 (5)	0·25	0·2833 (5)	8·8
O(12)	0·3592 (4)	0·25	0·4591 (5)	7·0
O(13)	0·2214 (5)	0·1266 (8)	0·4118 (5)	11·1
Cl(2)	0·14554 (11)	0·25	0·79061 (13)	4·4
O(21)	0·1301 (6)	0·25	0·8989 (5)	11·7
O(22)	0·2448 (5)	0·25	0·7694 (7)	9·7
O(23)	0·1075 (4)	0·1268 (5)	0·7375 (4)	8·9
Complex (2)				
Cu	0·75781 (11)	0·04873 (6)	0·22757 (5)	3·5
N(1)	0·7738 (8)	0·0431 (5)	0·3589 (4)	4·3
C(2)	0·7553 (12)	−0·0318 (6)	0·4055 (5)	5·3
N(3)	0·7689 (9)	−0·0119 (6)	0·4942 (4)	5·6
C(4)	0·8014 (12)	0·0784 (7)	0·5028 (6)	6·1
C(5)	0·8061 (12)	0·1125 (6)	0·4196 (6)	5·5
C(6)	0·7565 (18)	−0·0792 (10)	0·5701 (8)	9·9
C(7)	0·659 (3)	−0·1468 (13)	0·5556 (11)	15·7
N(11)	0·6031 (9)	0·1545 (5)	0·2160 (5)	5·3
C(12)	0·5708 (12)	0·1819 (7)	0·1225 (6)	5·9
C(13)	0·6217 (16)	0·1141 (9)	0·0637 (6)	8·8
N(14)	0·7331 (11)	0·0513 (5)	0·0935 (5)	6·1
C(15)	0·7918 (15)	−0·0286 (8)	0·0578 (6)	7·8
C(16)	0·8992 (14)	−0·0819 (7)	0·1140 (7)	6·8
N(17)	0·8960 (9)	−0·0617 (5)	0·2083 (5)	5·2
Cl(1)	1·0852 (3)	0·20613 (13)	0·17635 (13)	4·4
O(11)	1·0034 (11)	0·1560 (7)	0·2353 (6)	10·4
O(12)	1·0965 (15)	0·1597 (8)	0·0986 (7)	13·4
O(13)	0·9892 (15)	0·2827 (7)	0·1552 (8)	13·6
O(14)	1·2295 (9)	0·2419 (7)	0·2155 (7)	10·1
Cl(2)	0·3769 (3)	−0·09607 (13)	0·21424 (13)	4·4
O(21)	0·5310 (13)	−0·0823 (12)	0·2242 (12)	18·6
O(22)	0·322 (2)	−0·0183 (9)	0·1719 (12)	20·2
O(23)	0·341 (3)	−0·1718 (7)	0·1651 (7)	16·6
O(24)	0·326 (3)	−0·1106 (9)	0·2936 (9)	19·4

* As defined by Hamilton (1959).

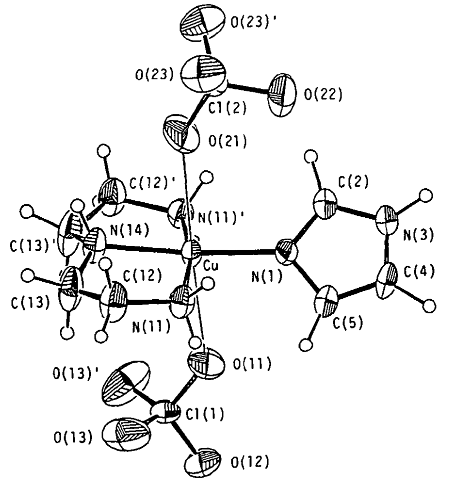

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the molecular structure of (1) showing the atomic numbering system. Non-H atoms are represented by thermal ellipsoids with 30% probability levels, whereas H atoms are drawn by a sphere with $B = 1{\cdot}0$ Å^2. Only one of the two disordered structures is drawn for the imidazole ligand (see text).

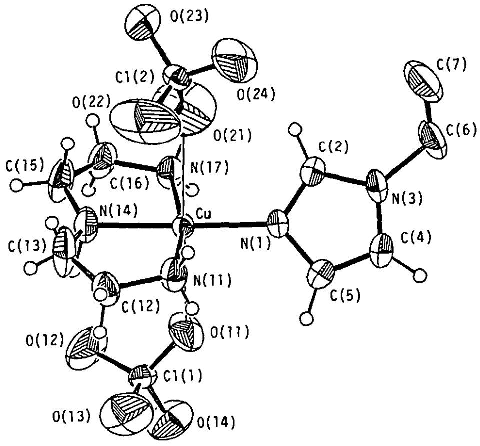

Fig. 2. *ORTEP*II drawing (Johnson, 1976) of the molecular structure of (2) showing the atomic numbering system. Atoms are represented with the same conditions as in Fig. 1.

1596 and 2859 reflections [$|F| > 3\sigma(|F|)$] used in the refinements of (1) and (2), respectively. Parameters refined 180 for (1) and 291 for (2). Final $R = 0{\cdot}061$ ($wR = 0{\cdot}086$, $S = 3{\cdot}6$) for (1) and $R = 0{\cdot}074$ ($wR = 0{\cdot}098$, $S = 1{\cdot}1$) for (2). Weighting scheme: $w = [\sigma(F_o)^2 + a|F_o| + b|F_o|^2]^{-1}$, with the weighting parameters $a = -0{\cdot}0021$ and $b = 0{\cdot}0022$ for (1), and $a = 0{\cdot}0143$ and $b = 0{\cdot}0005$ for (2). $(\Delta/\sigma)_{max}$ for non-H atoms 0·71 for (1) and 0·08 for (2). Max. and min. $\Delta\rho$ peaks +0·7 and −0·5 e Å^{-3} for (1) and +0·8 and −0·5 e Å^{-3} for (2).

All the computations were done on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. Final atomic parameters are listed in Table 1. Bond distances and angles are presented in Table 2.* Perspective views of the molecular structures of (1) and (2) are depicted in Figs. 1 and 2, respectively. The relatively high R value for (2) may be partly caused by the large thermal motion of the perchlorate anions. The structures of both complexes are similar to each other. The geometry around the Cu atom in each complex is octahedral, with the Cu coordinated by three N atoms of the dien ligand, an N atom of the imidazole ligand and two O atoms of the perchlorate anions. The crystallographic mirror plane passes through the Cu, N(1), N(14), O(11), Cl(1), O(12), O(21), Cl(2) and O(22) atoms in (1). The imidazole group, therefore, occupies two positions related by the mirror plane, only one of which is shown in Fig. 1. Distances between the Cu and O atoms are much longer than the usual covalent bond lengths. The O atoms of the ClO_4 anion are semicoordinated at the apical sites to the Cu atom. In both complexes, the Cu—O(11) bonds are significantly longer than the Cu—O(21) bonds [0·19 Å for (1) and 0·12 Å for (2)]. The Cu atom and four N atoms at the equatorial sites are approximately coplanar in each complex, the maximum deviations of the N atoms from the least-squares planes being 0·13 and 0·04 Å for (1) and (2), respectively. Bond lengths and angles in the dien ligand and between the Cu atom and the ligand are normal. The planes of the imidazole groups are inclined

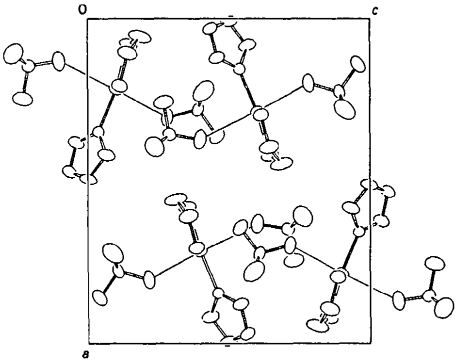

Fig. 3. *ORTEP*II drawing (Johnson, 1976) of crystal structure packing in the unit cell of (1) as viewed along the b axis. Non-H atoms are represented by thermal ellipsoids with 30% probability levels, whereas H atoms are omitted for clarity. Only one of the two disordered imidazole structures is shown (see text).

Table 2. *Bond distances* (Å) *and bond angles* (°) *for non*-H *atoms*

	(1)	(2)		(1)	(2)		(1)	(2)
Cu—N(1)	1·970 (5)	1·971 (7)	N(3)—C(4)	1·328 (23)	1·349 (13)	C(16)—N(17)		1·452 (14)
Cu—N(11)	2·006 (4)	2·009 (7)	N(3)—C(6)		1·518 (17)	Cl(1)—O(11)	1·398 (7)	1·375 (10)
Cu—N(14)	2·012 (7)	2·011 (9)	C(4)—C(5)	1·324 (19)	1·351 (14)	Cl(1)—O(12)	1·422 (6)	1·363 (12)
Cu—N(17)		2·016 (8)	C(6)—C(7)		1·28 (3)	Cl(1)—O(13)	1·409 (7)	1·396 (13)
Cu—O(11)	2·571 (6)	2·570 (10)	N(11)—C(12)	1·473 (7)	1·466 (12)	Cl(1)—O(14)		1·394 (10)
Cu—O(21)	2·763 (8)	2·685 (18)	C(12)—C(13)	1·443 (10)	1·417 (16)	Cl(2)—O(21)	1·354 (9)	1·295 (18)
N(1)—C(2)	1·297 (13)	1·316 (12)	C(13)—N(14)	1·392 (10)	1·354 (16)	Cl(2)—O(22)	1·418 (9)	1·362 (18)
N(1)—C(5)	1·397 (14)	1·376 (12)	N(14)—C(15)		1·390 (16)	Cl(2)—O(23)	1·426 (6)	1·350 (18)
C(2)—N(3)	1·336 (22)	1·362 (13)	C(15)—C(16)		1·411 (17)	Cl(2)—O(24)		1·318 (20)
N(1)—Cu—N(11)	96·3 (2)	96·1 (3)	Cu—N(1)—C(5)	125·3 (7)	128·9 (6)	C(15)—C(16)—N(17)		114·2 (10)
N(1)—Cu—N(14)	174·2 (3)	177·6 (4)	C(2)—N(1)—C(5)	105·4 (8)	106·4 (8)	Cu—N(17)—C(16)		111·2 (6)
N(1)—Cu—N(17)		96·9 (3)	N(1)—C(2)—N(3)	111·2 (12)	110·0 (8)	Cu—O(11)—Cl(1)	136·1 (4)	137·0 (6)
N(11)—Cu—N(14)	84·1 (3)	83·6 (4)	C(2)—N(3)—C(4)	107·2 (16)	107·6 (8)	Cu—O(21)—Cl(2)	144·8 (5)	143·3 (12)
N(11)—Cu—N(17)	166·2 (2)^a	166·4 (3)	C(2)—N(3)—C(6)		126·5 (9)	O(11)—Cl(1)—O(12)	109·9 (4)	111·3 (7)
N(14)—Cu—N(17)		83·2 (4)	C(4)—N(3)—C(6)		125·9 (9)	O(11)—Cl(1)—O(13)	108·2 (4)	105·6 (7)
O(11)—Cu—O(21)	177·6 (3)	172·0 (5)	N(3)—C(4)—C(5)	108·4 (14)	107·0 (9)	O(11)—Cl(1)—O(14)		112·5 (6)
O(11)—Cu—N(1)	84·0 (2)	89·7 (3)	N(1)—C(5)—C(4)	107·8 (11)	109·0 (9)	O(12)—Cl(1)—O(13)	110·5 (4)	106·4 (8)
O(11)—Cu—N(11)	87·8 (2)	92·2 (3)	N(3)—C(6)—C(7)		116·8 (15)	O(12)—Cl(1)—O(14)		115·4 (7)
O(11)—Cu—N(14)	101·8 (3)	92·7 (4)	Cu—N(11)—C(12)	110·5 (4)	110·9 (6)	O(13)—Cl(1)—O(14)	109·5 (4)^c	104·6 (7)
O(11)—Cu—N(17)		91·8 (3)	N(11)—C(12)—C(13)	111·3 (5)	111·7 (9)	O(21)—Cl(2)—O(22)	109·8 (6)	102·3 (11)
O(21)—Cu—N(1)	93·6 (3)	88·7 (5)	C(12)—C(13)—N(14)	115·6 (7)	119·9 (11)	O(21)—Cl(2)—O(23)	113·2 (5)	111·4 (11)
O(21)—Cu—N(11)	92·5 (2)	95·8 (5)	Cu—N(14)—C(13)	109·8 (5)	110·7 (8)	O(21)—Cl(2)—O(24)		108·1 (12)
O(21)—Cu—N(14)	80·6 (3)	89·0 (5)	Cu—N(14)—C(15)		111·3 (8)	O(22)—Cl(2)—O(23)	106·4 (5)	112·1 (11)
O(21)—Cu—N(17)		80·6 (5)	C(13)—N(14)—C(15)	128·0 (7)^b	133·9 (11)	O(22)—Cl(2)—O(24)		116·0 (12)
Cu—N(1)—C(2)	128·9 (6)	124·7 (6)	N(14)—C(15)—C(16)		117·2 (11)	O(23)—Cl(2)—O(24)	107·3 (4)^d	106·9 (12)

Notes: (*a*) N(11)—Cu—N(11)′, (*b*) C(13)—N(14)—C(13)′, (*c*) O(13)—Cl(1)—O(13)′, (*d*) O(23)—Cl(2)—O(23)′.

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* Lists of H-atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42897 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

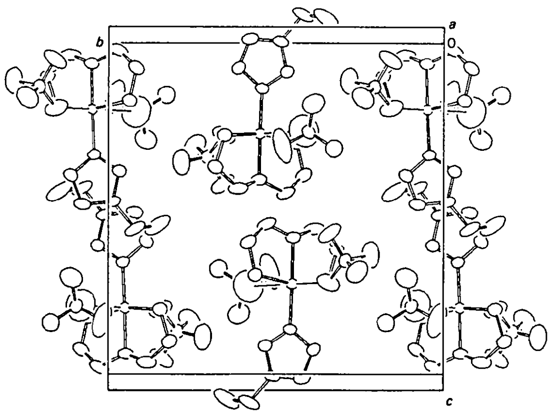

Fig. 4. *ORTEP*II drawing (Johnson, 1976) of crystal structure packing in the unit cell of (2) as viewed along the a^* axis. Atoms are represented with the same conditions as in Fig. 3.

at 47·6 and 48·9° to the copper equatorial planes for (1) and (2), respectively. The Cu—N(1) bond lengths in the present complexes are slightly shorter than the corresponding Cu—N distances in the octahedral copper–imidazole complexes $[Cu(ImH)_4(NO_3)_2]$ (average 2·011 Å) (McFadden, McPhail, Garner & Mabbs, 1976) and $[Cu(ImH)_6](NO_3)_2$ (average 2·031 Å) (McFadden, McPhail, Garner & Mabbs, 1975). Bonding geometries in the imidazole ligand in each complex are essentially the same as those of the above complexes.

Crystal structures of (1) and (2) are presented in Figs. 3 and 4, respectively. No abnormally short intermolecular contacts are observed in either of the complexes. The shortest interatomic distances between non-H atoms are 3·01 (2) Å [O(23)(x, y, z)···N(3)($-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$)] for (1), and 3·23 (2) Å [O(12)(x, y, z)···C(15)($2-x, -y, -z$)] for (2), both of which are observed in the contacts between the cationic complex and the anion.

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Bis-μ-[methylenebis(dimethylphosphine)]digold(I) Dichloride Dihydrate and its Comparison with the Diphenylphosphine Analogue

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Abstract. $[Au_2(C_5H_{14}P_2)_2]Cl_2.2H_2O$, $M_r = 773·10$, triclinic, $P\bar{1}$, $a = 7·943$ (3), $b = 10·043$ (4), $c = 7·884$ (3) Å, $\alpha = 105·14$ (3), $\beta = 109·16$ (3), $\gamma = 66·06$ (3)°, $V = 537$ Å^3, $Z = 1$, $D_m = 2·34$, $D_x = 2·39$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 141·7$ cm^{-1}, $F(000) = 360$, $T = 298$ K, $R = 0·058$ for 2551 observed reflections. The compound was synthesized according to Ludwig & Meyer [*Helv. Chim. Acta* (1982), **65**, 934–943]. The molecule consists of dimeric units with linear coordination of the Au atoms [P—Au—P angles of 176·61 (5)°]; there is distinct metal–metal interaction [Au—Au distance = 3·010 (1) Å]. The Cl$^-$ ions are only associated, unlike in the analogous compound bis-μ-[methylenebis(diphenylphosphine)]digold(I) dichloride, where they are bound covalently. An explanation for this difference is presented.

Introduction. Binuclear gold(I) phosphine complexes are interesting primarily for two reasons: (i) the various coordination numbers and geometries found in them; (ii) the frequently observed metal–metal interactions (Schmidbaur, Wohlleben, Schubert, Frank & Huttner,

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