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[1,1′-Diphenyl-3,3′-(ethylenediimino)di-1-butanonato]copper(II), [Cu($C_{22}H_{22}N_2O_2$)] and [1,1′-Diphenyl-3,3′-(ethylenediimino)di-1-butanonato]palladium(II), [Pd($C_{22}H_{22}N_2O_2$)]

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Abstract. Cu compound (I): $M_r = 409{\cdot}97$, monoclinic, $P2_1/n$, $a = 10{\cdot}971$ (4), $b = 7{\cdot}878$ (2), $c = 21{\cdot}972$ (4) Å, $\beta = 96{\cdot}31$ (2)°, $V = 1887{\cdot}47$ Å^3, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}2$ cm^{-1}, $F(000) = 852$, $T = 298$ (2) K. Pd compound (II): $M_r = 452{\cdot}83$, monoclinic, $P2_1/n$, $a = 10{\cdot}066$ (2), $b = 7{\cdot}903$ (1), $c = 21{\cdot}806$ (3) Å, $\beta = 96{\cdot}43$ (1)°, $V = 1894{\cdot}99$ Å^3, $Z = 4$, $D_x = 1{\cdot}59$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 77{\cdot}6$ cm^{-1}, $F(000) = 920$, $T = 298$ (2) K. Final R values are 0·055 (I) and 0·042 (II) for 2213 and 3120 observed $[F_o > 3\sigma(F_o)]$ reflections, respectively. The compounds are isostructural and show square-planar coordination around the metals. The structures agree well with those of the Co^{II} and Ni^{II} complexes and show similar changes in the ligand bond lengths, compared with the free ligand, caused by coordination to the metal.

Introduction. Metal complexes of tetradentate Schiff-base ligands such as *N,N′*-ethylenebis(acetylacetonimine) and *N,N′*-ethylenebis(salicylideneimine) have been widely studied because of their unusual properties (Calligaris, Nardin & Randaccio, 1972). But studies on the metal complexes of the related base *N,N′*-ethylenebis(benzoylacetonimine), $C_{22}H_{24}N_2O_2$, appear to be limited, and this prompted us to start work in this field. We described earlier the structures of the free base, $C_{22}H_{24}N_2O_2$ (Haider, Hashem, Malik & Hursthouse, 1981), and the cobalt(II) complex, [Co($C_{22}H_{22}N_2O_2$)] (Haider, Hashem, Malik & Hursthouse, 1980), and now report the structural studies of the Cu^{II} and Pd^{II} derivatives. The structure of the corresponding Ni^{II} complex has been determined by Malatesta & Mugnoli (1981).

Experimental. Title complexes were prepared by reacting *N,N′*-ethylenebis(benzoylacetonimine) with cupric chloride and palladium chloride, respectively, in methanol; brick-red prisms (I) and light-yellow needles (II) suitable for X-ray work obtained by recrystallization from methanol/dichloromethane. D_m not measured. Cell parameters from least-squares refinement of setting angles for 25 reflections [$14 < \theta(\text{Mo } K\alpha) < 16°$ for (I) and $28 < \theta(\text{Cu } K\alpha) < 32°$ for (II)] automatically centered on Enraf–Nonius CAD-4 diffractometer. Intensity data recorded on same instrument following standard procedures (Jones, Hursthouse, Malik & Wilkinson, 1979). 3 standard intensities, monitored every 1 h of exposure time, showed minor fluctuations. Semi-empirical absorption corrections applied to both data sets using ψ-scan values of three reflections in each case. Further experimental information is given in Table 1. Structures determined by heavy-atom method; least-squares refinement on F with all non-H anisotropic converged at $R = 0{\cdot}0547$, $R_w = 0{\cdot}0679$, $S = 1{\cdot}923$ (I), and $R = 0{\cdot}0419$, $R_w = 0{\cdot}0633$, $S = 3{\cdot}850$ (II) for 2213 and 3120 observed $[F_o > 3\sigma(F_o)]$ reflections, respectively. $w = k/[\sigma^2(F_o) + gF_o^2]$ with $\sigma(F_o)$ from counting statistics. H atoms located from difference maps not refined, but included in calculation of F_c with common $U_{\text{iso}} = 0{\cdot}05$ Å^2. Highest peaks in final difference maps 0·74 e Å^{-3} (I) and 0·71 e Å^{-3} (II) in vicinity of metal atoms and without stereochemical significance. Analyses of variance showed no systematic trend with $\sin\theta$, F_o or indices. Calculations performed on VAX 11/750 computer using *SHELX*80 (Sheldrick, 1980), *XANADU*

Table 1. *Experimental details*

	Cu complex	Pd complex
Crystal size (mm)	0·55 × 0·27 × 0·08	0·60 × 0·11 × 0·07
Transmission min., max.	0·837, 0·996	0·548, 0·997
θ_{min}, θ_{max} (°)	1·5, 25	3, 75
Range of h	−13→13	−13→13
k	0→9	0→9
l	0→26	0→25
Scan mode	ω–2θ	ω–2θ
ω-scan width (°)	0·85 + 0·35 tanθ	0·85 + 0·15tanθ
ω-scan speed (° min^{-1})	1·67–6·67	1·67–6·67
Total data measured	3826	4162
Total unique data	3307	3595
Total observed data $[F_o > 3\sigma(F_o)]$	2213	3120
R_{int}(from merging intensity controls and equivalents)	0·0081	0·0072
Parameters refined	244	244
Δ/σ(max.)	0·001	0·068
Parameters k and g in weighting scheme	1·6295, 0·0012	2·0811, 0·0003

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(Roberts & Sheldrick, 1975) and *SNOOPI* (Davies, 1983). Neutral-atom scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for non-H and H atoms, respectively; f' and f'' for Cu and Pd from Cromer & Liberman (1970). The final atomic parameters and bond lengths and angles are given in Tables 2 and 3.* The molecular structure and molecular packing in the unit cell are shown for the Pd compound in Figs. 1 and 2, respectively.

Table 2. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}[U_{11} + U_{22} + U_{33}].$$

	x	y	z	U_{eq}
Cu complex				
Cu	5124·9 (6)	2945·7 (9)	5332·5 (3)	33·0
O(1)	3945 (3)	2713 (5)	5907 (2)	51
O(2)	6179 (3)	3925 (6)	5984 (2)	53
N(1)	4087 (4)	1863 (6)	4678 (2)	46
N(2)	6330 (4)	3129 (6)	4762 (2)	47
C(1)	2877 (5)	2034 (7)	5796 (2)	44
C(2)	2374 (5)	1414 (9)	5247 (3)	54
C(3)	2997 (5)	1309 (8)	4700 (3)	50
C(4)	4734 (5)	1541 (8)	4129 (3)	56
C(5)	5826 (6)	2721 (9)	4124 (3)	58
C(6)	7461 (5)	3657 (8)	4878 (3)	51
C(7)	7950 (5)	4212 (8)	5468 (3)	54
C(8)	7322 (4)	4379 (7)	5975 (3)	44
C(9)	2283 (6)	417 (9)	4164 (3)	68
C(10)	8304 (6)	3742 (10)	4380 (3)	72
C(11)	2173 (5)	1918 (7)	6349 (2)	44
C(12)	1125 (5)	934 (8)	6368 (3)	59
C(13)	521 (5)	864 (9)	6890 (3)	67
C(14)	965 (5)	1792 (9)	7401 (3)	63
C(15)	1997 (6)	2772 (9)	7394 (3)	61
C(16)	2602 (5)	2849 (8)	6867 (3)	52
C(17)	7918 (5)	5121 (7)	6553 (2)	44
C(18)	9172 (5)	5288 (8)	6680 (3)	58
C(19)	9694 (5)	6023 (10)	7218 (3)	67
C(20)	8958 (6)	6594 (8)	7643 (3)	65
C(21)	7704 (6)	6433 (9)	7534 (3)	60
C(22)	7189 (5)	5680 (8)	6994 (3)	50
Pd complex				
Pd	5151·2 (3)	2974·9 (4)	5335·0 (1)	31·8
O(1)	3925 (3)	2803 (5)	5936 (2)	41
O(2)	6220 (3)	4051 (5)	6022 (1)	39
N(1)	4130 (4)	1858 (5)	4668 (2)	37
N(2)	6356 (4)	3086 (5)	4749 (2)	37
C(1)	2869 (4)	2082 (7)	5806 (2)	49
C(2)	2424 (5)	1417 (8)	5248 (2)	60
C(3)	3026 (5)	1316 (7)	4696 (2)	54
C(4)	4782 (6)	1493 (8)	4120 (2)	61
C(5)	5864 (5)	2695 (8)	4120 (2)	64
C(6)	7468 (5)	3622 (7)	4879 (2)	56
C(7)	7952 (4)	4239 (7)	5477 (2)	57
C(8)	7344 (4)	4435 (6)	5983 (2)	49
C(9)	2320 (6)	427 (8)	4151 (2)	69
C(10)	8340 (6)	3681 (9)	4385 (3)	80
C(11)	2146 (4)	1989 (7)	6351 (2)	54
C(12)	1107 (5)	1016 (9)	6350 (3)	70
C(13)	485 (5)	947 (10)	6870 (3)	78
C(14)	902 (6)	1846 (10)	7393 (3)	81
C(15)	1916 (6)	2847 (10)	7392 (3)	74
C(16)	2541 (5)	2889 (8)	6880 (2)	61
C(17)	7965 (4)	5233 (7)	6559 (2)	49
C(18)	9230 (5)	5387 (9)	6670 (3)	72
C(19)	9750 (5)	6127 (11)	7211 (3)	86
C(20)	9042 (6)	6684 (9)	7658 (3)	75
C(21)	7797 (6)	6518 (9)	7552 (3)	71
C(22)	7276 (5)	5777 (7)	7016 (2)	58

Table 3. *Selected bond lengths* (Å) *and angles* (°)

	Cu complex	Pd complex
M–O(1)	1·913 (5)	1·994 (5)
M–O(2)	1·902 (6)	1·992 (5)
M–N(1)	1·932 (6)	1·950 (6)
M–N(2)	1·924 (6)	1·950 (6)
C(1)–O(1)	1·287 (7)	1·303 (7)
C(8)–O(2)	1·306 (7)	1·292 (6)
C(3)–N(1)	1·280 (8)	1·302 (8)
C(6)–N(2)	1·307 (8)	1·301 (8)
C(4)–N(1)	1·486 (8)	1·491 (7)
C(5)–N(2)	1·485 (8)	1·452 (8)
C(2)–C(1)	1·361 (8)	1·367 (8)
C(8)–C(7)	1·378 (8)	1·364 (7)
C(3)–C(2)	1·449 (9)	1·441 (8)
C(7)–C(6)	1·417 (9)	1·439 (8)
C(11)–C(1)	1·513 (9)	1·507 (9)
C(17)–C(8)	1·482 (8)	1·501 (8)
C(9)–C(3)	1·513 (10)	1·519 (9)
C(10)–C(6)	1·509 (9)	1·525 (8)
C(5)–C(4)	1·518 (10)	1·528 (10)
O(2)–*M*–O(1)	86·7 (2)	85·7 (2)
N(2)–*M*–N(1)	86·5 (3)	85·0 (3)
N(1)–*M*–O(1)	93·6 (3)	94·6 (3)
N(2)–*M*–O(2)	93·1 (3)	94·7 (3)
N(1)–*M*–O(2)	177·7 (2)	178·3 (2)
N(2)–*M*–O(1)	178·6 (2)	178·7 (2)
C(1)–O(1)–*M*	125·6 (4)	123·1 (4)
C(8)–O(2)–*M*	127·2 (4)	123·1 (4)
C(3)–N(1)–*M*	126·8 (5)	125·6 (4)
C(6)–N(2)–*M*	127·1 (5)	124·8 (4)
C(4)–N(1)–*M*	112·6 (4)	113·2 (4)
C(5)–N(2)–*M*	112·8 (4)	113·5 (4)
C(4)–N(1)–C(3)	120·2 (6)	120·9 (5)
C(6)–N(2)–C(5)	120·0 (5)	121·3 (5)
C(2)–C(1)–O(1)	126·1 (6)	126·0 (5)
C(7)–C(8)–O(2)	123·5 (6)	126·3 (5)
C(11)–C(1)–O(1)	114·0 (5)	113·1 (5)
C(17)–C(8)–O(2)	115·4 (5)	113·4 (5)
C(11)–C(1)–C(2)	119·8 (6)	121·0 (5)
C(17)–C(8)–C(7)	121·1 (5)	120·2 (5)
C(3)–C(2)–C(1)	125·0 (6)	127·7 (6)
C(8)–C(7)–C(6)	126·6 (6)	127·2 (6)
C(2)–C(3)–N(1)	122·7 (6)	123·0 (6)
C(7)–C(6)–N(2)	122·1 (5)	123·7 (5)
C(9)–C(3)–N(1)	122·3 (6)	121·3 (6)
C(10)–C(6)–N(2)	121·2 (6)	120·9 (6)
C(9)–C(3)–C(2)	115·0 (6)	115·6 (6)
C(10)–C(6)–C(7)	116·7 (6)	115·4 (6)
C(5)–C(4)–N(1)	110·4 (5)	109·2 (5)
C(4)–C(5)–N(2)	109·7 (5)	110·0 (5)

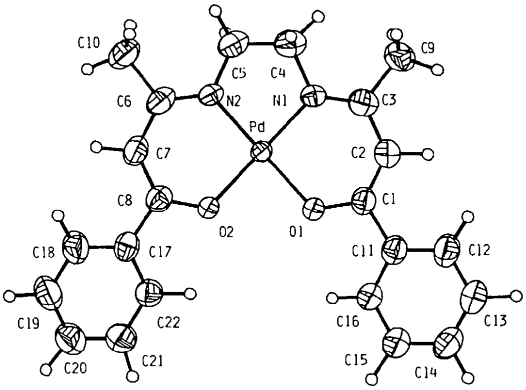

Fig. 1. A general view of the molecular structure of [$Pd(C_{22}H_{22}N_2O_2)$]. The H atoms are represented by open circles of arbitrary radius; other atoms by thermal ellipsoids with 50% probability.

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* Lists of structure factors, anisotropic thermal parameters, coordinates, bond lengths and angles involving H atoms, dimensions of the phenyl rings, and results of least-squares plane and dihedral angle calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39733 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

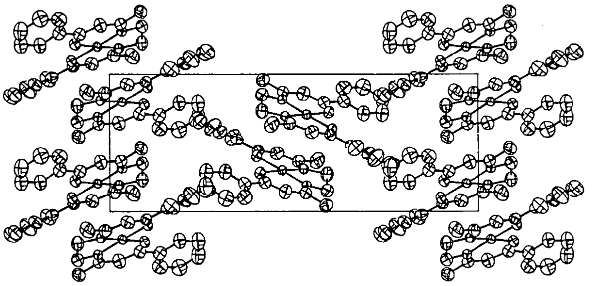

Fig. 2. A view along **a** of the packing of molecules in the unit cell. The H atoms are omitted for clarity.

Discussion. The Cu^{II} and Pd^{II} compounds are isostructural with the corresponding Co^{II} (Haider, Hashem, Malik & Hursthouse, 1980) and Ni^{II} (Malatesta & Mugnoli, 1981) derivatives. The metal atoms in a square-planar arrangement lie within 0·031 (4) Å (I) and 0·026 (4) Å (II) of the mean plane of the N_2O_2 atoms. The O/N—M—O/N angles (*cis*) in the square plane are within 5° of the ideal value of 90°. The M—N and M—O bonds are virtually identical in the Co^{II} and Ni^{II} compounds [Co—O = 1·855 (4), 1·847 (4); Co—N = 1·866 (4), 1·861 (4); Ni—O = 1·851 (4), 1·858 (4); Ni—N = 1·852 (4), 1·859 (4) Å], but longer (by ~0·06 Å) in the Cu^{II} and (by ~0·12 Å) in the Pd^{II} derivatives, as expected from the relative atomic-radii difference.

As in the case of other tetradentate Schiff-base complexes (Calligaris, Nardin & Randaccio, 1972), the dimensions of the ligand in the present series are independent of the nature of the metal and it shows extensive delocalization. However, compared with the free ligand (Haider, Hashem, Malik & Hursthouse, 1981) the bonds in the chelate rings in all four compounds are systematically modified. The changes in ligand bonds, effected by metal coordination, although small (<0·06 Å), are real. The N(1)—C(4)—C(5)—N(2) torsion angles are 30·5 (7)° in (I) and 32·6 (7)° in (II). The O(1)—C(1)—C(11)—C(16) and O(2)—C(8)—C(17)—C(22) torsion angles showing the non-planarity of the phenyl rings with the respective chelate rings are 13·6 (7) and −16·1 (7) and 10·9 (7) and −12·2 (7)°, in (I) and (II), respectively. All these values are comparable with those in the Co^{II} and Ni^{II} compounds.

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Structure of Trisodium Fructose 1,6-Diphosphate Octahydrate, $3Na^+.C_6H_{11}O_{12}P_2^{3-}.8H_2O$

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Abstract. $M_r = 550{\cdot}2$, monoclinic, $P2_1$, $a = 7{\cdot}085$ (1), $b = 11{\cdot}645$ (3), $c = 13{\cdot}290$ (3) Å, $\beta = 102{\cdot}26$ (1)°, $U = 1071{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}708$, $D_x = 1{\cdot}704$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 3{\cdot}311$ mm^{-1}, $F(000) = 572$, $T = 300$ K, final R for 2303 unique reflections is 0·055. The phosphate residues at the 1 and 6 positions have

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