Metal Complexes of Sexidentate Ligands derived from 3-Ethoxymethylenepentane-2,4-dione: Reactions with Aliphatic Diamines and Crystal Structures of [3,3′-Ethylenedithiobis(*o*-phenyleneiminomethylidyne)bis(pentane-2,4-dionato)(2−)]-nickel(II) and -copper(II)

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Potentially sexidentate ligands with $[N_2S_2O_2]^{2-}$, $[N_4O_2]^{2-}$, and $[N_2O_4]^{2-}$ donor sets have been prepared from reactions of 3-ethoxymethylenepentane-2,4-dione with 1,2-di(*o*-aminophenylthio)ethane, 1,2-di(*o*-aminoanilino)-ethane, and 1,2-di(*o*-aminophenoxy)ethane. Six-co-ordinate nickel(II) and copper(II) complexes of 3,3′-ethylenedithiobis(*o*-phenyleneiminomethylidyne)bis[pentane-2,4-dionate(2−)] (4a) and (5a) and of 3,3′-ethylenedi-iminobis(*o*-phenyleneiminomethylidyne)bis[pentane-2,4-dionate(2−)] have been characterized and their reactions with ethylenediamine and other diamines have been examined. These result in ligand rearrangement to quadridentate dianionic systems, rather than in formation of cyclic sexidentate ligands. *X*-Ray structure determination of (4a), space group $P2_1/c$, $a = 8.963(4)$, $b = 29.067(10)$, $c = 9.935(3)$ Å, $\beta = 106.02(1)°$, $Z = 4$, and isomorphous (5a), $a = 8.887(3)$, $b = 28.825(11)$, $c = 10.168(4)$ Å, $\beta = 106.51(2)°$ (heavy-atom method, 1 677 and 2 452 four-circle diffractometer data, R 0.056 and 0.060 respectively), shows the ligand to define an irregular octahedral arrangement of donors with the two terminal keto-groups in *cis* co-ordination sites, suitably positioned for intramolecular reaction with aliphatic diamines.

RELATIVELY few sexidentate macrocyclic ligands are known which form stable complexes with transition-metal ions.[1] In certain cases such complexes can be isolated[2,3] directly from Schiff-base condensation reactions when these are carried out in the presence of transition-metal ions (Scheme 1). A route to a related group of sexidentate ligands would be available if the cyclization reactions developed by Jaeger[4] (Scheme 2) could be modified by incorporation of an additional pair of donor atoms into either of the chains R^1 or R^2, by using diamine precursors of the type (1).

In this paper we report the syntheses and structural properties of the complexes (4) and (5), and the results of treating these with aliphatic diamines in an attempt

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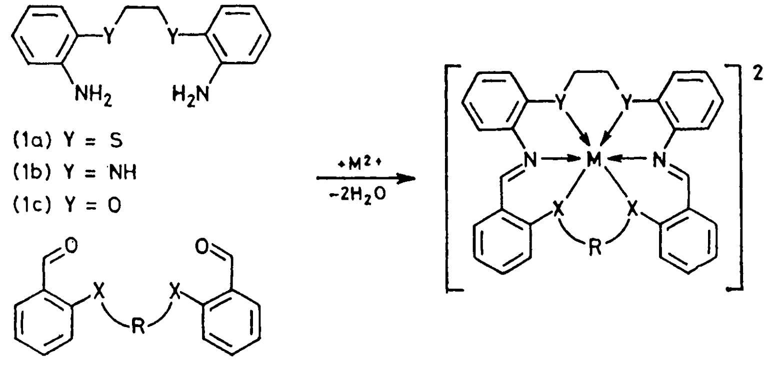
[1] D. St. C. Black and J. A. Hartshorn, *Co-ordination Chem. Rev.*, 1973, **9**, 219.

[2] P. A. Tasker and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1970, **92**, 7072.

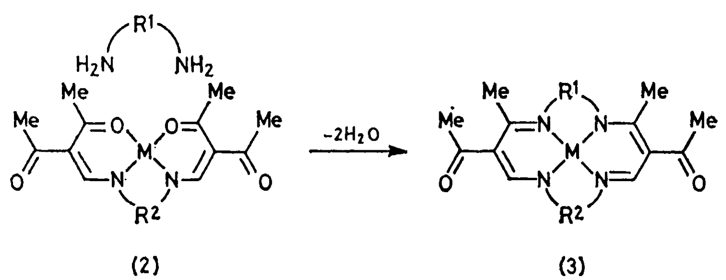
[3] L. F. Lindoy and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 4690.

[4] (*a*) E. Jaeger, *Z. Chem.*, 1964, **4**, 437; 1968, **8**, 392, 470; *Z. anorg. Chem.*, 1969, **364**, 177; (*b*) *Z. anorg. Chem.*, 1966, **346**, 76.

to obtain complexes of macrocyclic sexidentate ligands.



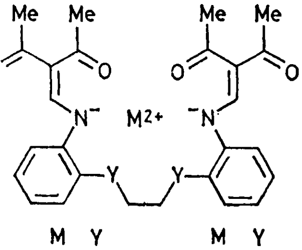
SCHEME 1



SCHEME 2

EXPERIMENTAL

Methods and Materials.—Chemicals were of reagent or equivalent grade. Mass spectra were determined using a Perkin-Elmer–Hitachi RMS4 and an A.E.I. MS50 instrument. Microanalysis data were obtained on a Perkin-Elmer 240 elemental analyzer. Infrared spectra were recorded on Perkin-Elmer 237 and Unicam SP 2000 spectrometers in both hexachlorobutadiene and Nujol mulls.



	M	Y		M	Y
(4a)	Ni	S	(4b)	Ni	NH
(5a)	Cu	S	(5b)	Cu	NH
(6a)	H_2	S	(6b)	H_2	NH
(6c)	H_2	O			

Preparations.—3-Ethoxymethylenepentane-2,4-dione was prepared by the method of ref. 5.

3,3′-*Ethylenedithiobis*(o-*phenyleneiminomethylidyne*)*bis*(*pentane*-2,4-*dione*) (6a). A solution of 3-ethoxymethylenepentane-2,4-dione (12.0 g) in methanol (10 cm³) was added dropwise to a refluxing, vigorously stirred, solution of 1,2-bis(*o*-aminophenylthio)ethane [6] (1a) (10.6 g) in methanol (25 cm³). The solid which separated was collected after cooling and recrystallized from 1,4-dioxan to give compound (6a) (11.5 g, 61%) as fine white needles, m.p. 193 °C (decomp.) (Found: C, 62.8; H, 5.8; N, 5.7. $C_{26}H_{28}N_2O_4S_2$ requires C, 62.9; H, 5.7; N, 5.6%); $\nu_{max.}$ at 3 150br, 3 070, 3 000, 2 920, 1 635, 1 598, 1 562, 1 540, 1 480, 1 450, 1 427, 1 397, 1 359, 1 350, and 1 325 cm⁻¹. Mass spectrum: principal peaks at *m/e* 496(12), 263(14), 262(81), 236(15), 235(64), 234(100), 220(42), 218(24), 217(59), 215(40), and 201(27%).

3,3′-*Ethylenedi-iminobis*(o-*phenyleneiminomethylidyne*)-*bis*(*pentane*-2,4-*dione*) (6b). A similar procedure using 1,2-bis(*o*-aminoanilino)ethane [2] (1b) in place of (1a) gave bright yellow needles of (6b), m.p. 191 °C (decomp.), yield 68% (Found: C, 67.4; H, 6.9; N, 12.1. $C_{26}H_{30}N_4O_4$ requires C, 67.5; H, 6.5; N, 12.1%); $\nu_{max.}$ at 3 330, 2 995, 2 930, 2 862, 1 625br, 1 592, 1 572, 1 520, 1 478, 1 463, 1 398, 1 350, and 1 312 cm⁻¹.

3,3′-*Ethylenedioxybis*(o-*phenyleneiminomethylidyne*)*bis*(*pentane*-2,4-*dione*) (6c). A similar procedure using 1,2-di(*o*-aminophenoxy)ethane [2] (1c) in place of (1a) gave pale yellow needles of (6c), m.p. 217 °C (decomp.), yield 72% (Found: C, 67.0; H, 6.1; N, 6.3. $C_{26}H_{28}N_2O_6$ requires C, 67.2; H, 6.1; N, 6.0%); $\nu_{max.}$ at 3 150w, 3 002, 2 960, 2 890, 1 660, 1 625, 1 590, 1 572, 1 508, 1 465, 1 407, 1 362, 1 356, 1 320, and 1 308 cm⁻¹. Mass spectrum: principal peaks at *m/e* 464(75), 421(11), 353(10), 246(19), 244(11), 230(16), 228(16), 204(50), 203(10), 202(31), and 201(14%).

[3,3′-*Ethylenedithiobis*(o-*phenyleneiminomethylidyne*)*bis*(*pentane*-2,4-*dionato*)(2−)]*nickel*(II) (4a). A solution of hydrated nickel(II) acetate (2.5 g) in methanol (50 cm³) was added dropwise to a boiling stirred suspension of the ligand (6a) (5.0 g) in 1,4-dioxan (50 cm³). After refluxing for 20 min the solution was cooled and the resulting dark green crystalline product was collected, washed with small

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[5] L. Claisen, *Annalen*. 1897, **297**, 1.

[6] R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1277.

volumes of cold methanol and diethyl ether, and dried in air to give (4a) (4.5 g, 82%), m.p. 288 °C (decomp.) (Found: C, 56.4; H, 5.2; N, 5.5. $C_{26}H_{26}N_2NiO_4S_2$ requires C, 56.4; H, 4.7; N, 5.1%); $\nu_{max.}$ at 3 086, 3 070, 3 000, 2 929, 1 654, 1 637, 1 600, 1 580br, 1 488, 1 395br, 1 355, 1 300, 1 270, and 1 212 cm^{-1}.

[3,3′-*Ethylenedi-iminobis*(o-*phenyleneiminomethylidyne*)-*bis*(*pentane*-2,4-*dionato*)(2—)]*nickel*(II) (4b). A similar procedure using a methanolic suspension of (6b) instead of (6a) gave (4b) as a light brown microcrystalline powder, m.p. 276 °C (decomp.), yield 89% (Found: C, 60.6; H, 5.8; N, 11.0. $C_{26}H_{28}N_4NiO_4$ requires C, 60.1; H, 5.4; N, 10.8%); $\nu_{max.}$ at 3 315, 3 030, 2 995, 2 972, 2 939, 2 922, 2 892, 1 642, 1 610, 1 580br, 1 495br, 1 420, 1 400br, 1 355, 1 302, 1 275, 1 259, 1 251, 1 220, and 1 202 cm^{-1}.

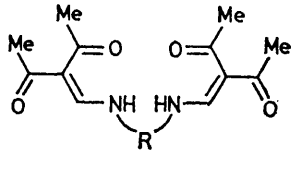
[3,3′-*Ethylenedithiobis*(o-*phenyleneiminomethylidyne*)*bis*-(*pentane*-2,4-*dionato*)(2—)]*copper*(II) (5a). Using hydrated copper(II) acetate in a procedure similar to that for (4a) above gave (5a) as brown-red prisms, m.p. 308 °C (decomp.), yield 86% (Found: C, 60.2; H, 4.9; N, 5.3. $C_{26}H_{26}CuN_2O_4S_2$ requires C, 55.95; H, 4.7; N, 5.0%); $\nu_{max.}$ at 3 080, 3 000, 2 928, 1 650, 1 640, 1 590br, 1 498, 1 490, 1 476, 1 390br, 1 402, 1 270, and 1 208 cm^{-1}.

[3,3′-*Ethylenedi-iminobis*(o-*phenyleneiminomethylidyne*)-*bis*(*pentane*-2,4-*dionato*)(2—)]*copper*(II) (5b). A similar procedure using a methanolic suspension of (6b) instead of (6a) gave (5b) as light green crystals, m.p. 206 °C (decomp.), yield 80% (Found: C, 60.1; H, 5.8; N, 11.0. $C_{26}H_{28}CuN_4O_4$ requires C, 59.6; H, 5.4; N, 10.7%); $\nu_{max.}$ at 3 328, 3 035, 2 992, 2 972, 2 922, 2 885, 1 641, 1 609, 1 580br, 1 498br, 1 468, 1 439, 1 400br, 1 352, 1 345, 1 299, 1 274, 1 262, 1 253, 1 218, and 1 203 cm^{-1}.

Reactions of (4) *and* (5) *with Ethylenediamine and Propane*-1,3-*diamine*.—(*i*) *No solvent*. The alkanediamine (0.5 cm^3) and (4) or (5) (1 mmol) were set aside in a sealed vessel at 40 °C. The reaction mixtures showed a series of colour changes [*e.g.* (4a) with ethylenediamine (en): green to red to orange] which was complete after 24 h. Water (1 cm^3) was added and the resulting precipitate was collected, washed with cold water, and dried *in vacuo* for 24 h. The i.r. spectra of the products indicated the presence of (1a) or (1b) which were separated from other products by recrystallization from toluene. Heating the reaction mixture under reflux produced a metallic deposit on the vessel and mixtures from which it was more difficult to isolate (1a) or (1b).

(*ii*) *In methanol*. Complexes (4) or (5) (1 mmol) were dissolved in the minimum volume of methanol. Ethylenediamine (2 mmol) was added and the reaction mixture set aside in a sealed vessel at room temperature. A series of colour changes [*e.g.* (5a) with en: brown to green to turquoise to dark blue] was complete after several weeks. Crystals of (2) which separated (in most cases after reducing the volume of solution by slow evaporation under a stream of nitrogen) were collected after 6 months, washed with a little methanol, dried *in vacuo*, and recrystallized from the solvents used in ref. 4*b*. Infrared, mass-spectral, and m.p. data were used to establish the identity of these materials with samples prepared by the methods of ref. 4*b*. When the reactions were attempted with suspensions of (4) or (5) in small volumes of methanol, unchanged (4) or (5) was detected after setting aside for several weeks.

Reaction of (6*c*) *with Ethylenediamine and Nickel*(II) *Acetate*.—Ethylenediamine (1 cm^3) was added to a stirred suspension of (6c) (0.5 g) and nickel(II) acetate in ethanol (40 cm^3). Heating under reflux for 30 min was accompanied by a colour change from purple to red. After evaporation to dryness an orange powder was obtained which was washed with water and dried *in vacuo*. The i.r. spectrum indicated the presence of (1c) and 3,3′-ethylenedi-iminodimethylidynebis(pentane-2,4-dione) (7; R = [CH_2]$_2$).



(7)

The latter was separated by recrystallization from ethanol and found to be identical to material prepared by the method of ref. 4*b*.

X-*Ray Crystallography*.—*Data collection*. Intensities were collected on a Philips PW1100 four-circle diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation (λ 0.710 7 Å). The parameters are summarized in Table 1. Data were collected for one hemisphere of reciprocal space ($l \geqslant 0$). Weak reflections were not measured if $[I_p - 2(I_p)^{\frac{1}{2}}] < I_b$ on a preliminary scan, where I_p is the intensity at the top of the reflection profile and I_b the mean of two 5-s background measurements on either side of the peak. The background measuring time was proportional to I_b/I_i, I_i being the intensity recorded in scanning the reflection. Three standard reflections measured at 6-h intervals during data collection showed no significant variations in intensity.

TABLE 1

Crystal data

	Complex (4a)	Complex (5a)
Formula	$C_{26}H_{26}N_2NiO_4S_2$	$C_{26}H_{26}CuN_2O_4S_2$
M	552.8	557.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	8.963(4)	8.887(3)
b/Å	29.067(10)	28.825(11)
c/Å	9.935(3)	10.168(4)
β/°	106.02(1)	106.51(2)
U/Å^3	2 487.8	2 497.3
Z	4	4
D_c/g cm^{-3}	1.48	1.48
D_m(by flotation)/g cm^{-3}	1.46	1.48
F(000)	1 144	1 156
μ(Mo-K_α)/cm^{-1}	9.19	10.14
Crystal size/mm	*ca.* 0.2 × 0.2 × 0.1	*ca.* 0.3 × 0.15 × 0.1
Reflections measured	3 546	6 047
Unique reflections	1 677	2 452
Scan width (ω)/°	0.90 + 0.10tanθ	0.74 + 0.05tanθ
Scan speed/° s^{-1}	0.05	0.05
θ range /°	$3.0 \leqslant \theta \leqslant 22.5$	$3.0 \leqslant \theta \leqslant 25.0$
R	0.056	0.060
R'	0.054	0.060
Least-squares parameters	170	170
Average shift-to-error	0.2	0.3
Maximum shift-to-error	2.9	2.3

The data were corrected for Lorentz and polarization factors but not for absorption; equivalents were averaged and reflections for which $I < 3\sigma(I)$ were rejected. The unit-cell dimensions were obtained by least-squares analysis from the setting angles of the 25 reflections used to calculate the UB matrix. The space group $P2_1/c$ was determined unambiguously from the systematic absences; $h0l$ with l odd, $0k0$ with k odd.

TABLE 2

Refined atomic positional parameters (× 10^4) *

(*a*) Nickel complex

Atom	*x*	*y*	*z*
Ni	416(1)	1 255(1)	−1 259(1)
S(1)	3 018(3)	1 226(2)	364(3)
S(2)	1 664(3)	1 437(1)	−3 061(3)
O(1)	−1 659(7)	1 191(2)	−2 715(6)
O(2)	−462(7)	1 194(2)	377(6)
O(3)	−2 551(10)	204(3)	−5 867(10)
O(4)	−3 436(10)	2 097(3)	1 534(9)
N(1)	738(8)	567(2)	−1 389(8)
N(2)	172(8)	1 941(2)	−1 170(8)
C(1)	−2 096(10)	877(3)	−3 616(10)
C(2)	−1 325(10)	456(3)	−3 562(10)
C(3)	−13(10)	319(3)	−2 431(10)
C(4)	1 915(10)	351(3)	−336(10)
C(5)	1 950(10)	−124(3)	−84(9)
C(6)	3 130(11)	−322(3)	943(11)
C(7)	4 332(11)	−48(3)	1 754(11)
C(8)	4 306(11)	418(3)	1 552(11)
C(9)	3 076(10)	618(3)	509(10)
C(10)	4 270(12)	1 344(3)	−757(11)
C(11)	3 588(11)	1 211(4)	−2 259(11)
C(12)	1 946(10)	2 027(3)	−2 611(10)
C(13)	2 983(11)	2 284(3)	−3 122(11)
C(14)	3 195(12)	2 745(4)	−2 801(11)
C(15)	2 341(11)	2 955(4)	−2 051(11)
C(16)	1 295(10)	2 695(3)	−1 504(10)
C(17)	1 096(10)	2 229(3)	−1 763(9)
C(18)	−825(10)	2 134(3)	−611(10)
C(19)	−1 609(10)	1 924(3)	290(10)
C(20)	−1 259(10)	1 478(3)	855(10)
C(21)	−3 853(12)	985(4)	−4 743(12)
C(22)	−1 913(13)	94(4)	−4 641(13)
C(23)	−1 675(14)	−402(4)	−4 642(13)
C(24)	−2 709(12)	2 237(4)	720(12)
C(25)	−2 948(14)	2 730(4)	261(14)
C(26)	−1 737(12)	1 310(4)	2 112(11)

(*b*) Copper complex

Atom	*x*	*y*	*z*
Cu	351(1)	1 268(0)	−1 359(1)
S(1)	3 247(2)	1 253(1)	188(2)
S(2)	1 567(3)	1 443(1)	−3 225(2)
O(1)	−1 875(6)	1 169(2)	−2 868(6)
O(2)	−489(5)	1 212(2)	309(6)
O(3)	−2 524(8)	122(2)	−5 823(8)
O(4)	−3 432(8)	2 146(2)	1 404(9)
N(1)	712(6)	597(2)	−1 456(6)
N(2)	144(6)	1 937(2)	−1 297(6)
C(1)	−2 198(8)	849(2)	−3 741(9)
C(2)	−1 333(8)	434(2)	−3 598(8)
C(3)	−27(7)	331(2)	−2 476(8)
C(4)	1 919(8)	382(2)	−397(8)
C(5)	1 853(8)	−90(2)	−81(8)
C(6)	3 021(8)	−288(3)	950(9)
C(7)	4 285(8)	−31(3)	1 689(9)
C(8)	4 347(8)	435(2)	1 428(9)
C(9)	3 166(8)	649(2)	382(8)
C(10)	4 318(9)	1 326(3)	−1 070(9)
C(11)	3 489(9)	1 183(3)	−2 516(10)
C(12)	1 906(8)	2 030(2)	−2 719(8)
C(13)	2 954(9)	2 289(3)	−3 215(9)
C(14)	3 192(9)	2 753(3)	−2 869(9)
C(15)	2 362(9)	2 957(3)	−2 068(9)
C(16)	1 320(8)	2 699(2)	−1 567(9)
C(17)	1 085(7)	2 227(2)	−1 880(8)
C(18)	−856(7)	2 141(2)	−752(8)
C(19)	−1 664(7)	1 949(2)	163(8)
C(20)	−1 291(8)	1 499(2)	731(8)
C(21)	−3 675(10)	928(3)	−4 936(10)
C(22)	−1 844(10)	45(3)	−4 591(11)
C(23)	−1 527(11)	−445(3)	−4 122(12)
C(24)	−2 731(10)	2 262(3)	585(10)
C(25)	−2 977(10)	2 760(3)	75(11)
C(26)	−1 800(10)	1 333(3)	1 957(10)

* The standard deviation of the least significant digit is included in parentheses in this and subsequent Tables.

Structure solution and refinement. The structures of (4a) and (5a) were solved by the heavy-atom method and refined using full-matrix least-squares procedures with the metal and sulphur atoms having anisotropic temperature factors. An attempt to refine the acetyl groups of the copper(II) complex using anisotropic thermal parameters was not pursued due to correlation between the resulting matrix elements in the least-squares process. All the hydrogen atoms were inserted in geometrically calculated positions (C–H 1.08 Å) and the methyl groups were refined as rigid bodies. Two separate isotropic temperature factors were determined for the hydrogen atoms, one for the methyl hydrogens [(4a) 0.11(2) $Å^2$, (5a) 0.14(2) $Å^2$] and one for the remaining hydrogens [(4a) 0.11(1) $Å^2$, (5a) 0.10(1) $Å^2$]. In the final stages of the refinement the reflections were weighted as $w = 1/\sigma^2(F_o)$. The *R* values are given in Table 1 and atomic co-ordinates in Table 2. Table 3 lists interatomic bond lengths and angles in the co-ordination sphere of the metals, and Table 4 interatomic contacts <2.7 Å. Thermal parameters, interatomic bond lengths and angles in the ligand, equations for least-squares planes, and final structure factors are given in Supplementary Publication No. SUP 22256 (21 pp.).*

TABLE 3

Interatomic bond lengths (Å) and angles (°) in the co-ordination spheres of the complexes

Atoms	Nickel complex	Copper complex
M–S(1)	2.443(3)	2.607(2)
N–S(2)	2.416(3)	2.488(3)
M–O(1)	2.026(6)	2.151(5)
M–O(2)	2.000(6)	2.044(5)
M–N(1)	2.029(7)	1.968(5)
M–N(2)	2.012(7)	1.941(5)
S(1)–M–S(2)	86.8(1)	84.0(1)
S(1)–M–O(1)	171.7(2)	165.1(1)
S(1)–M–O(2)	88.8(2)	91.7(1)
S(1)–M–N(1)	83.2(2)	82.4(2)
S(1)–M–N(2)	95.8(2)	94.8(2)
S(2)–M–O(1)	90.7(2)	89.6(2)
S(2)–M–O(2)	171.1(2)	171.5(1)
S(2)–M–N(1)	93.7(2)	92.8(2)
S(2)–M–N(2)	83.9(2)	83.6(2)
O(1)–M–O(2)	94.7(2)	95.9(2)
O(1)–M–N(1)	89.0(3)	94.5(2)
O(1)–M–N(2)	91.9(3)	94.5(2)
O(2)–M–N(1)	93.4(3)	93.9(2)
O(2)–M–N(2)	88.9(3)	89.5(2)
N(1)–M–N(2)	177.5(3)	175.6(2)

TABLE 4

Intermolecular contacts <2.7 Å, excluding H–H contacts

	Complex	
Atoms [a]	(4a)	(5a)
H(14) · · · $O(4^{I})$	2.37(1)	2.41(1)
H(7) · · · $O(3^{II})$	2.45(2)	2.43(3)
H(5) · · · $O(2^{III})$	2.58(1)	2.69(1)
H(8) · · · $O(3^{II})$	2.67(2)	[2.88(3)] [b]
H(6) · · · $O(1^{III})$	[2.74(1)] [b]	2.64(1)
H(25) · · · $O(4^{IV})$	[2.80(1)] [b]	2.61(1)

[a] Hydrogen atoms are given the number of the carbon atom to which they are attached and the second atom is related to the positions given in Table 2 by the operations: I $1 + x, \frac{1}{2} - y, z - \frac{1}{2}$; II $1 + x, y, 1 + z$; III $-x, -y, -z$; IV $x, \frac{1}{2} - y, z - \frac{1}{2}$. [b] Included for comparison.

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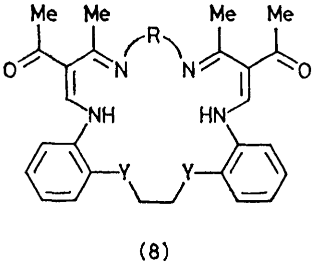
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

All computations were performed using the SHELX programs (Dr. G. M. Sheldrick). Scattering factors and anomalous-dispersion corrections for copper and nickel were taken from refs. 7 and 8.

RESULTS AND DISCUSSION

The potentially sexidentate ligands (6) were readily isolated from reactions of 3-ethoxymethylenepentane-2,4-dione with the appropriate aromatic diamine (1) in refluxing methanol, and the nickel(II) and copper(II) complexes (4) and (5) were obtained from the metal(II) acetates. Under comparable conditions, complexes of (6c) could not be obtained, probably because the ether groups provide poor donor atoms for transition-metal ions. Formulation of (4) and (5) as neutral six-co-ordinate complexes is supported by i.r. spectral data which are consistent with proton loss and shift of $C=O$ and $C=N$ stretching vibrations to lower energies on complex formation; this is confirmed for (4a) and (5a) by *X*-ray structure determination (see below).

The reactions of the sexidentate complexes with aliphatic diamines were studied initially under conditions which had been used previously by Jaeger [4] to effect the cyclization of the quadridentate systems shown in Scheme 2, *i.e.* by heating the linear complexes in anhydrous ethylenediamine (en) and propane-1,3-diamine (pd). Examination of the i.r. spectra of solid products showed that in such reactions the complexes [(4) or (5)] had been completely consumed, and in all cases the diamine precursors [either (1a) or (1b)] for the sexidentate ligands had been liberated. The displacement of (1a) or (1b) by the aliphatic diamines resulted in the formation of complexes of quadridentate ligands [(2) or (3)] and in some cases in the free quadridentate ligand (7). The relative yields of these products depend on the nature of (4) or (5) and on variations of reaction and work-up conditions. Small quantities of metallic nickel or copper were produced in some of the reactions. No evidence could be obtained for the formation of complexes of the cyclic sexidentate ligand (8).

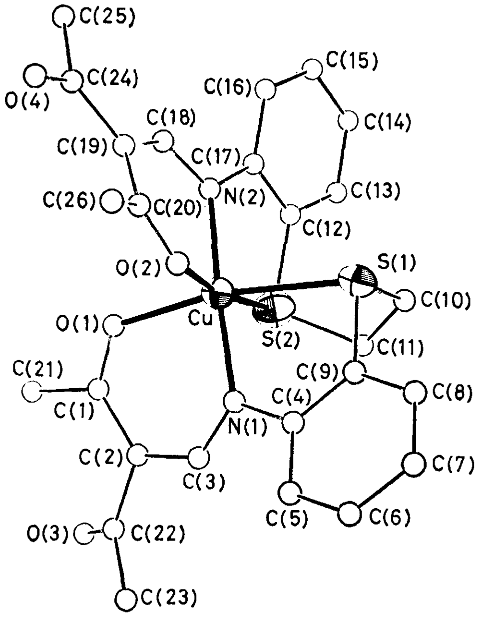


(8)

A striking series of colour changes accompanied each reaction, both when carried out as above, and under milder conditions using methanolic solutions of (4) and (5) and lower concentrations of en. In all the latter cases, when the reactions were allowed to go to completion the displacement of the aromatic diamines (1a) and (1b) was detected. Under these conditions the four-co-ordinate complexes (2) were the only other major products of the reaction. It was observed that reaction of the copper complexes (5a) and (5b) went to completion more rapidly than those of the nickel complexes (4a) and (4b). Attempts to isolate the highly coloured intermediates were unsuccessful.

The diamine precursor (1c) for (6c) was liberated when the latter was treated with alcoholic solutions of en and nickel(II) or copper(II) acetate.

A structure determination of the copper(II) complex (5a) was undertaken to establish whether steric features associated with the ligand may account for the failure to give the macrocyclic complex. The determination confirmed that the complex is six-co-ordinate (Figure), and showed it to have an isomeric form (9) in which the two unsaturated sections of the ligand span three meridional sites, rather than as in isomers (10)—(12). The arrangement of donor atoms is considerably distorted from a regular octahedron. The idealized isomer (9) has a two-fold rotation axis passing through the metal and the midpoint between the sulphur donor atoms, but in (5a) the co-ordinate bonds from equivalent S and O donors in the two halves of the ligand have significantly different lengths (Table 3), and atoms C(10) and C(11) of the ethane bridge between the sulphur atoms are displaced by unequal distances (0.151 and 0.769 Å) to the same side of the plane defined by atoms Cu, S(1), and S(2).



Complex (5a), showing the atom-labelling scheme

The irregularity of the co-ordination geometry of (5a) must result in part from the electronic requirements of the copper(II) ion, since the comparable nickel(II) complex (4a) shows much smaller deviations from two-fold symmetry (see Table 3 and supplementary material).

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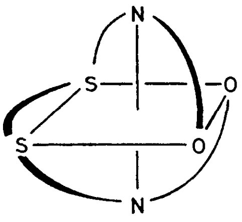
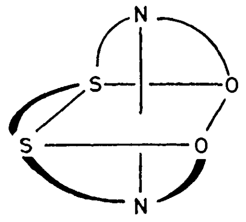
[7] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[8] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

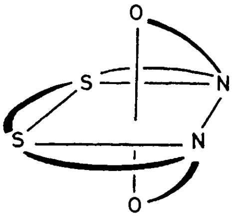
No abnormally short intermolecular contacts are observed in either complex (Table 4).



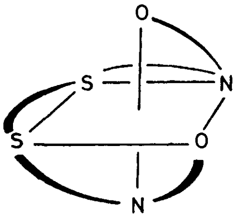
(9)



(10)



(11)



(12)

In the copper(II) complex (5a) three donor atoms O(1), N(1), and S(1) in one limb of the ligand form longer co-ordinate bonds than those in the other limb, although the difference between the Cu–N bond lengths is close to the significance level. The displacement of the donor atoms from the vertices of a regular octahedron does not fit into conventional schemes [9] for the description of co-ordination polyhedra of copper(II) complexes, and it is suggested that this form of distortion may result from constraints imposed by the multidentate nature of the ligand. A more flexible sexidentate ligand, 1,10-bis-(salicylideneamino)-4,7-dithiadecane, which also provides an $[N_2S_2O_2]^{2-}$ donor set, has recently been shown [10] to give pseudo-octahedral cobalt(III) complexes of isomeric types (9) and (11) in which no differences were detected between lengths of chemically equivalent co-ordinate bonds.

A comparison between the structure of (4a) and (5a) suggests that the bonding of the imine nitrogen atoms to the metal in (5a) (mean Cu–N 1.955 Å) is stronger than in (4a) (mean Ni–N 2.095 Å). This observation is consistent with the greater reactivity of the copper complexes in processes which involve attack at the imine carbon atom (see above), given the importance of metal-ion activation in similar types of reaction.[11]

The distance between the terminal keto-oxygen donor atoms in (4a) and (5a) [2.96(1) and 3.11(3) Å respectively] could be spanned readily in a five- or six-membered chelate ring derived from en or pd. Although this appears to allow formation of the macrocyclic ligands (8) it takes no account of the steric requirements of the resulting imino-nitrogen donor atoms, about which the most favourable disposition of bonds would lie approximately in the planes defined by the unsaturated β-iminoamine chelate rings. Such requirements present severe steric difficulties in a cyclic ligand giving a 'wrap-around' isomer analogous to (9). This source of instability may militate against the formation of the sexidentate macrocycle under conditions where imine formation and cleavage is rapid and the reactions are subject to thermodynamic control. Under such circumstances the favoured products are likely to be the 'strain-free' complexes (2) and (3).

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[7/1669 *Received, 21st September,* 1977]

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