la série des complexes tris(nitroso-1 ethanal oximato), outre $[P(C_6H_5)_4][FeL_3]$ et $[As(C_6H_5)_4][FeL_3]$, $[N(n\text{-}C_4H_9)_4][MnL_3]$ cristallise sous forme de conglomérat d'énantiomères (groupe spatial $P2_1$); par contre $[N(n\text{-}C_4H_9)_4][CoL_3]$ cristallise sous forme de racémate (groupe spatial $C2/c$; Gouzerh, Jeannin, Miler-Srenger & Valentini, 1979).

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Structure of Disodium 1,4-Piperazinedicarbodithioate Hexahydrate, $2Na^+.C_6H_8N_2S_4^{2-}.6H_2O$

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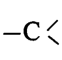
Abstract. $M_r = 390{\cdot}5$, monoclinic, $P2_1/c$, $a = 6{\cdot}009\,(2)$, $b = 12{\cdot}185\,(2)$, $c = 11{\cdot}494\,(4)$ Å, $\beta = 92{\cdot}47\,(2)°$, $V = 840{\cdot}8\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}52\,(2)$, $D_x = 1{\cdot}54$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}57$ mm^{-1}, $F(000) = 404$, $T = 293$ K, $R = 0{\cdot}021$, $R_w = 0{\cdot}036$ for 1917 unique reflections and 128 variable parameters. Sodium coordinates five water molecules and one sulphur atom forming a distorted octahedron. Such coordination polyhedra share edges to build parallel files running along **a** and linked together by the 1,4-piperazinedicarbodithioate anions into layers parallel to the *ac* plane. The 1,4-piperazinedicarbodithioate anion exhibits the chair conformation and is made up of two almost planar C_2NCS_2 moieties related by a centre of symmetry. The S—C—S bite angle is 119·6 (1)°. The C—S distances are not equivalent: 1·740 (1) and 1·713 (1) Å; the shorter corresponds to the S···Na interaction and one S···H—O hydrogen bond while the longer corresponds to four S···H—O hydrogen bonds.

Introduction. Potentially bisbidentate ligands are suitable for synthesizing monodimensional transition-metal complexes liable to display unusual magnetic behaviour. The dithiooxalate anion $O_2C_2S_2^{2-}$ has already given such complexes and, among them, the first ordered magnetic bimetallic chains (Gleizes & Verdaguer, 1981). Changing the geometry of the ligand would modify the coupling between magnetic centres and hopefully lead to a modulation of the magnetic properties. Bisbidentate ligands with two  $-C\langle{}^{S}_{S}$ bite

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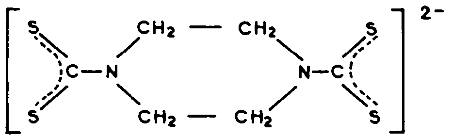
groups have been selected first. The piperazinebis(dithiocarbamate) anion (IUPAC name: 1,4-piperazinedicarbodithioate)



has given homo- and heterometallic complexes with a number of transition metals (Troy, Legros & Galy, 1984); their study is in progress. The present paper reports the structure of the starting material: disodium piperazinebis(dithiocarbamate) hexahydrate, $Na_2[S_2CN(CH_2)_4NCS_2].6H_2O$.

Experimental. Synthesis from piperazine, CS_2 and NaOH in relative proportions 1:2:2 in a mixture of 2-propanol and diethyl ether (Preti, Tosi & Zannini, 1979; Zaidi, Khan & Neelam, 1980); recrystallization from mixture of methanol and diethyl ether; D_m by the neutral buoyancy method in chloroform–carbon tetrachloride mixture; colourless block-like crystal 0·4 × 0·35 × 0·3 mm, systematic absences from precession photographs: $h0l$, l odd and $0k0$, k odd, space group $P2_1/c$; cell dimensions from least-squares fit to the θ angles of 25 reflections measured on the diffractometer in the range $11 < \theta < 24°$, absorption corrections unnecessary because of shape of crystal and small μ; details of data collection and refinement given in Table 1; scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations performed with *SHELX* (Sheldrick, 1976), illustrations with *ORTEP* (Johnson, 1965); hydrogen atoms located on Fourier difference map, methylenic H atoms given a common C—H bond length and common isotropic temperature factor (both values refined), H atoms of water molecules treated in the same way; weighting scheme adjusted to make variance of $w(\Delta F)^2$ independent of magnitude of $|F_o|$, final max. $\Delta/\sigma < 0·006$ for non-hydrogen-atom parameters, six of seven highest peaks of final difference map ($0·35 < \Delta\rho < 0·22$ e Å^{-3}) situated in the middle of a covalent bond and ascribable to an asphericity effect, min. peak height of map −0·22 e Å^{-3}.

Discussion. Final positional and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2.* Selected bond lengths and angles are given in Table 3.

Table 1. *Data collection and refinement*

Diffractometer: Enraf–Nonius CAD-4
Maximum Bragg angle: $\theta_{max} = 29°$, $(\sin\theta/\lambda)_{max} = 0·682$ Å^{-1}
$-8 \le h \le 8, 0 \le k \le 16, 0 \le l \le 15$
Standard reflections: 0,14,0, 008, 520, 30$\bar{4}$
periodicity: 3600 s
maximum relative intensity variation <0·02
Number of measured reflections: 2435
Number of observed unique reflections: 1917
Number of unobserved reflections: 346
Criterion for unobserved reflections: $I < 2\sigma(I)$, $\sigma(I)$ estimated from a fast pre-scan.
Scan mode: $\omega/2\theta$, variable speed technique
pre-scan speed: 10° min^{-1} in ω
$\sigma(I)/I$ for final scan: 0·015
max. time for final scan: 90 s
min. scan speed: 1° min^{-1} in ω
scan width: $0·8 + 0·35 \tan\theta$ in ω
Standard deviation on structure factor amplitudes:
$\sigma(|F_o|) = \sigma_c(I)/2|F_o|Lp$
Lp: Lorentz–polarization factor
$\sigma_c(I)$ based on counting statistics
Solution of structure by Patterson method
Full-matrix least-squares refinement based on F
Function minimized: $\sum w(\Delta F)^2$
Weighting scheme: $w = 2·83/(\sigma^2|F_o| + 0·0002|F_o|^2)$
Secondary extinction correction of the form
$|F_{corr}| = |F_o|(1–0·0001\,x|F_o|^2/\sin\theta)$ with $x = 0·016$ (1)
Number of parameters refined: 128
Final reliability indices: $R = 0·021$; $R_w = 0·036$

Table 2. *Positional and equivalent isotropic thermal parameters for the non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Na	0·25130 (8)	0·03749 (4)	0·06623 (5)	0·0385
S(1)	0·66035 (5)	0·19793 (2)	0·30402 (2)	0·0291
S(2)	0·53733 (5)	−0·03759 (2)	0·27009 (2)	0·0310
N	0·7948 (2)	0·03502 (7)	0·44636 (8)	0·0269
C(1)	0·6765 (2)	0·06186 (8)	0·34952 (9)	0·0230
C(2)	0·8231 (2)	−0·07822 (9)	0·4881 (1)	0·0288
C(3)	0·9339 (2)	0·11153 (9)	0·5163 (1)	0·0283
O(1)	0·5918 (2)	0·12677 (7)	0·02190 (7)	0·0373
O(2)	0·9587 (2)	−0·08754 (9)	0·11216 (9)	0·0432
O(3)	0·1458 (2)	0·18707 (9)	0·1752 (1)	0·0462

Table 3. *Selected distances* (Å) *and angles* (°)

Symmetry code: (i) $2 - x, y, 1 - z$; (ii) $1 - x, -y, -z$; (iii) $x - 1, y, z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $1 + x, y, z$; (vi) $2 - x, y - \frac{1}{2}, \frac{1}{2} + z$; (vii) $1 - x, -y, 1 - z$

Piperazinebis(dithiocarbamate) anion			
C(1)—S(1)	1·740 (1)	N—C(2)	1·469 (1)
C(1)—S(2)	1·713 (1)	N—C(3)	1·469 (1)
C(1)—N	1·335 (1)	C(2)—C(3^{i})	1·518 (2)
C—H	0·949 (7)		
S(1)—C(1)—S(2)	119·6 (1)	C(1)—N—C(3)	124·8 (1)
S(1)—C(1)—N	120·3 (1)	C(2)—N—C(3)	111·2 (1)
S(2)—C(1)—N	120·1 (1)	N—C(2)—C(3^{i})	109·8 (1)
C(1)—N—C(2)	123·6 (1)	N—C(3)—C(2^{i})	109·7 (1)
Sodium coordination polyhedron			
Na—S(2)	2·990 (1)	Na—O(2^{ii})	2·439 (1)
Na—O(1)	2·391 (1)	Na—O(2^{iii})	2·402 (1)
Na—O(1^{ii})	2·450 (1)	Na—O(3)	2·316 (1)
O—H	0·772 (8)		
Hydrogen bonds			
S(1)···O(1)	3·366 (1)	S(1)···O(3^{v})	3·329 (2)
S(1)···O(1^{iv})	3·331 (1)	S(2)···O(2)	3·236 (1)
S(1)···O(3)	3·372 (2)		

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39194 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Sodium is coordinated to five water O atoms and one S atom forming a distorted octahedron. The octahedra related by the centres of symmetry share edges to build parallel files running along **a** (Fig. 1). The files are linked by the piperazinebis(dithiocarbamate) anions and form layers parallel to the *ac* plane (Figs. 1 and 2). The layers are held together by S···H—O hydrogen bonds.

The piperazinebis(dithiocarbamate) anion (Fig. 3) exhibits the chair conformation. It is made up of two almost planar $C_2NCS_2^-$ moieties related by a centre of symmetry: both N and C(1) atoms have a planar environment but the two planes are rotated to each other by 5·3 (1)°. Distances to the least-squares plane through S(1), S(2), C(1), N, C(2) and C(3) are: S(1) −0·007 (1), S(2) 0·015 (1), C(1) −0·009 (3), N −0·042 (2), C(2) 0·002 (3), C(3) 0·037 (3) Å. In the ring, bond lengths and angles are consistent with single C—C and C—N bonds, while outside the ring the C—N and C—S bonds have partial double-bond character indicating delocalization over the NCS_2^- system. The S(1) atom accepts four S···H—O hydrogen bonds and the S(2) atom accepts one S···H—O hydrogen bond and interacts with the sodium atom; the S···O and S···Na distances are given in Table 3. The C(1)—S(1) and C(1)—S(2) bond lengths are significantly different. The shorter one involves the S(2) atom which interacts with the Na atom. This is quite unusual and opposite to the common observation on sodium dithiocarbamates such as $Na[S_2CN(CH_3)_2].2H_2O$ (Oskarsson & Ymén, 1983), $Na[S_2CN(C_2H_5)_2].3H_2O$ (Colapietro, Domenicano & Vaciago, 1968) or $Na[S_2CN(CH_2)_4].2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980). Since the S···Na distance is of the same magnitude in all these compounds as well as in the title compound, the four S(1)···H—O hydrogen bonds must be responsible for the lengthening of the C(1)—S(1) bond. In this respect one may note that in $Na\{S_2CN[CH(CH_3)_2]_2\}.5H_2O$ (Ymén, 1983*b*) one of the S atoms accepts four hydrogen bonds and the C—S bond length is 1·745 (6) Å while the other S atom accepts two hydrogen bonds and the C—S bond length is 1·703 (6) Å (none of the S atoms interacts with the Na atom). Such a comparison emphasizes the weakness of the S···Na interaction in the dithiocarbamate salts and thus the C—S bond lengths are mainly affected by the number of hydrogen bonds accepted by the S atoms.

Since the C(1) atom is surrounded by three bonds with partial double-bond character, the bond angles around C(1) are very close to 120°. In contrast, the N atom is surrounded by one partial double bond [N—C(1)] and two single bonds [N—C(2) and N—C(3)]; thus the C(2)—N—C(3) angle is markedly smaller than the other two. This is a common feature of the dithiocarbamates cited before as well as dithiocarbamates with organic cations (Wahlberg, 1978, 1979).

As suggested by Ymén (1983*a*), in the dithiocarbamates with weak anion–cation interaction (*i.e.* with alkali metal or organic cations) the S—C—S bite angle is probably mainly affected by intramolecular S···H steric interactions. This is difficult to ascertain from X-ray data alone since the H position is poorly defined.

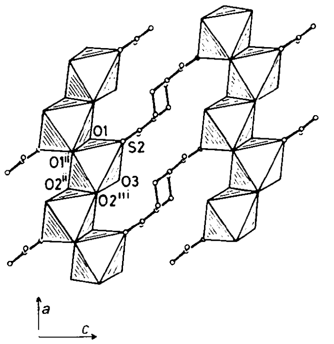

Fig. 1. Sodium coordination octahedra linked by piperazinebis(dithiocarbamate) anions form layers parallel to the *ac* plane.

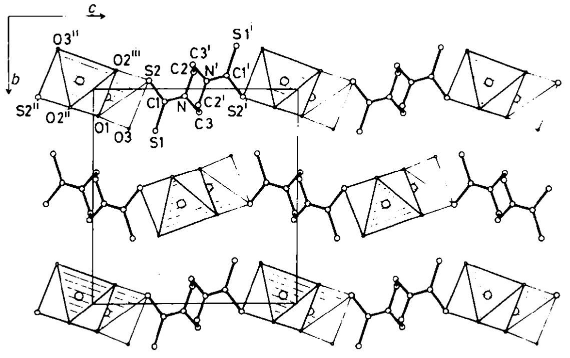

Fig. 2. Projection of the structure along **a**. Hydrogen atoms and hydrogen bonds omitted for the sake of clarity.

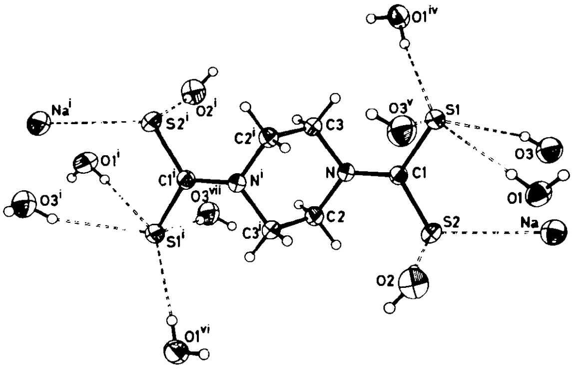

Fig. 3. The piperazinebis(dithiocarbamate) anion; 50% thermal ellipsoids; arbitrary thermal spheres for hydrogen atoms.

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Digold(III) Strontium Octaacetate Dihydrate, $Au_2Sr(C_2H_3O_2)_8.2H_2O$*

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Abstract. $M_r = 989{\cdot}94$, monoclinic, $C2/c$, $a = 12{\cdot}332\ (4)$, $b = 11{\cdot}487\ (4)$, $c = 19{\cdot}496\ (8)$ Å, $\beta = 101{\cdot}97\ (3)°$, $U = 2701{\cdot}7$ Å^3, $Z = 4$, $D_x = 2{\cdot}43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 128$ cm^{-1}, $F(000) = 1856$, room temperature, $R = 0{\cdot}065$ for 2703 observed reflections. The structure consists of isolated $SrAu_2(CH_3COO)_8$ units with crystallographic symmetry 2. Coordination geometry is square planar and Archimedean antiprismatic respectively at Au and Sr. Each acetate ion bridges Au and Sr. The C—O bond lengths indicate covalent Au—O but electrostatic Sr—O interactions. The water molecules occupy 'holes' in the lattice without forming hydrogen bonds.

Introduction. Little is known about carboxylate complexes of gold; simple carboxylates of the form AuX and AuX_3 appear to be unknown, and only the triphenylphosphine complexes Ph_3PAuX (X = acetate, formate, trifluoroacetate; Nichols & Charleston, 1969) have been characterized. We have begun a systematic study of gold carboxylate complexes and I here report the structure of the strontium salt $SrAu_2ac_8$ (ac = acetate), which crystallizes as the dihydrate. Details of the preparation of this and other compounds of general formula MAu$_2$ac$_8$.xH$_2$O (M = divalent metal cation) will be reported elsewhere.

Experimental. Crystal 0·4 × 0·35 × 0·2 mm mounted in glass capillary, 4760 profile-fitted intensities (Clegg, 1981) measured on Stoe–Siemens four-circle diffractometer ($2\theta_{max}$ 60°, monochromated Mo $K\alpha$ radiation); 3 standard reflections decreased gradually in intensity by *ca* 5% and the data were scaled accordingly; empirical absorption corrections (azimuthal scans; transmissions 0·28–0·72); averaging equivalents gave 3924 unique reflections (R_{int} 0·049), 2703 with $F > 4\sigma(F)$ used for all calculations; intensity distribution corresponded to pseudo-F-centring; cell constants refined from 2θ values of 40 reflections in the range 20–23°; structure solution by heavy-atom method; refinement on F to $R = 0{\cdot}065$, $R_w = 0{\cdot}068$ [Au and Sr anisotropic, H not located; 83 parameters, $w^{-1} = \sigma^2(F) + 0{\cdot}00055\,F^2$, $S = 1{\cdot}91$], max. Δ/σ 0·001; max. and min. heights in final $\Delta\rho$ map +2 (near Au), −3 e Å^{-3};† calculations performed with *SHELXTL* (Sheldrick, 1978); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates and bond lengths and angles are given in Tables 1 and 2. The structure is

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* Carboxylate and Related Complexes of Gold. Part 1.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39206 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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