the above-mentioned dicopper(II) complex, is remarkably longer than the values reported for other μ-hydroxo-dicopper(II) complexes, where values of 2·87 and 2·97 (Crawford, Richardson, Wasson, Hodgson & Hatfield, 1976) and 3·00 Å (Hoskins & Whillans, 1975) were found. This large separation is very probably due to the steric requirements of the organic ligand molecule of the title compound.

Some short contacts are found between O atoms of water molecules: O(3)···O(2) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$) = 2·87 (2) Å, and between the chloride anion and another water molecule: O(4)···Cl(3) ($-x$, $\frac{1}{2} + y$, $-z - \frac{1}{2}$) = 3·11 (2) Å, and O(4)···Cl(3) ($x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$) = 3·15 (1) Å.

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Aquabis(2,2'-bipyridyl)bis(thiocyanato-N)calcium, [Ca(C10H8N2)2(SCN)2(H2O)], and catena-Bis(2,2'-bipyridyl)-bis-μ-(thiocyanato-S,N)-barium, [Ba(C10H8N2)2(SCN)2]

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Abstract. [Ca(C10H8N2)2(SCN)2(H2O)]: $M_r = 486\cdot6$, monoclinic, $P2_1/c$, $a = 16\cdot33$ (1), $b = 9\cdot851$ (3), $c = 14\cdot802$ (7) Å, $\beta = 97\cdot91$ (5)°, $V = 2358$ (2) Å^3, $Z = 4$, $D_x = 1\cdot370$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·402 mm^{-1}, λ (Mo $K\alpha$) = 0·71069 Å, room temperature, $F(000) = 1008$. A block-diagonal least-squares refinement based on 1838 reflections led to R and R_w values of 7·6 and 4·8%, respectively. [Ba(C10H8N2)2(SCN)2]: $M_r = 565\cdot86$, monoclinic, $C2/c$, $a = 17\cdot047$ (7), $b = 10\cdot127$ (5), $c = 14\cdot371$ (4) Å, $\beta = 116\cdot61$ (3)°, $V = 2218$ (2) Å^3, $Z = 4$, $D_x = 1\cdot695$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·933 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, room temperature, $F(000) = 1112$. Full-matrix least-squares refinement based on 1381 reflections led to R and R_w values of 6·6 and 3·5%, respectively. The Ca^{2+} ion is seven-coordinate with the four pyridyl and two thiocyanate N atoms and one water molecule forming a distorted monocapped trigonal prism. The discrete molecules are held together by van der Waals types of interactions. The Ba^{2+} ion is eight-coordinate with six N atoms and two S atoms from thiocyanate groups of an adjacent molecule forming a distorted square antiprism.

The structure consists of long chains with thiocyanate groups bridging the Ba^{2+} ions.

Introduction. Weak interactions involving compounds normally found in biological systems have been of interest in our laboratories. We are investigating weak interactions between crown ethers and small neutral organic molecules as models for understanding secondary interactions that occur at biological receptor sites and enzyme pockets (Vögtle, Sieger & Müller 1981; Weber & Vögtle, 1981; Vögtle & Weber, 1980). These interactions may be of importance in stereoselective recognition by receptors and substrates. The coordination of alkali and alkaline-earth metals by N donors is also of interest in these studies.

Experimental. MeOH/ethyl acetate solutions of Ca(SCN)₂ and Ba(SCN)₂ were added to solutions of bipyridyl in a 1:2 ratio. The recovered Ca complex was recrystallized from acetone while the Ba complex was recrystallized from ethyl acetate. Intensity data collected on a Syntex $P2_1$ diffractometer system, $\theta:2\theta$ scanning technique, variable scan speed, Mo $K\alpha$ radiation, graphite monochromator. Room-temperature

lattice parameters were refined by a least-squares procedure utilizing 15 reflections whose angles were measured by a centering routine associated with the diffractometer. A Ca-complex crystal $0.38 \times 0.25 \times 0.11$ mm and a Ba-complex crystal $0.25 \times 0.25 \times 0.20$ mm were selected for X-ray measurements. Periodically monitored reflections (044, 006 for Ca; 204 for Ba) showed no significant changes in intensities. Of the 3965 independent reflections measured for the Ca complex ($2 \theta \le 50°$; $h \le 17$, $k \le 10$, $-15 \le l \le 15$), 1838 had intensities greater than $3\sigma (I)$; systematic absences ($l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$) consistent with space group $P2_1/c$. Of the 1509 independent reflections measured for the Ba complex ($2 \theta \le 45°$; $h \le 18$, $k \le 10$, $-14 \le l \le 14$), 1381 had intensities greater than $3\sigma(I)$; systematic absences ($h + k = 2n + 1$ for hkl, $l = 2n + 1$ for $h0l$) consistent with space groups Cc and $C2/c$. Lorentz and polarization corrections applied, no absorption corrections. The direct-methods program $MULTAN78$ (Main, Lessinger, Woolfson, Germain & Declercq, 1978) was used to solve both structures. Phases for the largest $|E|$ values were calculated and the phase sets with the highest combined figures of merit produced E maps which revealed the positions of most nonhydrogen atoms; the remainder of the nonhydrogen atoms were located in difference Fourier maps. H-atom positions were calculated; their contributions were included in the structure factor calculations, but the parameters were not refined. The Ca complex was refined by a block-diagonal least-squares technique while the Ba structure utilized a full-matrix refinement. Refinement was terminated when R_w became stationary. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. R, R_w and S are 0.076, 0.048 and 3.05 for the Ca complex and 0.066, 0.035 and 2.85 for the Ba complex. Maximum shift, last cycle: 0.70σ(Ca), 0.27σ (Ba). Atomic scattering factors calculated by the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); anomalous-scattering terms from *International Tables for X-ray Crystallography* (1974); locally written programs used for data reduction and block-diagonal least-squares calculations, $MULTAN78$ for direct-methods computations and XRAY76 for all others. Atomic positional parameters and U_{eq} values for the Ca complex are presented in Table 1 while those for the Ba complex are given in Table 2.* Bond distances and angles are in Table 3.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the Ca complex. The Ca^{2+} ion is seven-

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38405 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordinate with the geometry around the ion best described as a distorted monocapped trigonal prism. The δ values for an ideal hard-sphere monocapped trigonal prism (C_{2v}) are 0, 0, 41.5 and 41.5° (Muetterties & Guggenberger, 1974) while the values observed for the Ca complex are 5.8, 7.0, 32.8 and 56.7°. The Ca—N(bipyridyl) distances vary from 2.506 (8) to 2.559 (8) Å with an average value of 2.53 Å. The Ca—N(thiocyanate) distances are 2.400 (8) Å and 2.478 (6) Å. The Ca—OH$_2$ distance is 2.432 (5) Å. The deviation from ideal C_{2v} symmetry is primarily related to restrictions imposed by the pyridyl ligand bite (N···N = 2.77 Å) and is reflected in the N—Ca—N angles which vary from 64 to 98°.

Table 1. *Atomic positional parameters ($\times 10^4$) and U_{eq} values ($\times 10^3$) for the Ca complex*

$$U_{eq} = \tfrac{1}{2}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ca(1)	7320 (1)	952 (1)	9774 (1)	39 (1)
N(1)	6909 (5)	2810 (7)	10659 (5)	58 (7)
N(2)	7984 (4)	45 (8)	11257 (4)	51 (6)
N(3)	5791 (5)	660 (10)	9194 (4)	42 (6)
N(4)	6789 (5)	−1453 (7)	9655 (5)	38 (6)
N(5)	8734 (6)	1982 (8)	9906 (5)	45 (6)
N(6)	8302 (5)	−97 (7)	8761 (4)	44 (6)
O(7)	7055 (2)	2429 (4)	8449 (3)	37 (4)
C(8)	6645 (5)	3556 (8)	11130 (6)	35 (8)
S(9)	6242 (1)	4596 (2)	11830 (1)	63 (2)
C(10)	8202 (5)	271 (10)	12011 (5)	74 (7)
S(11)	8499 (1)	537 (3)	13075 (1)	74 (2)
C(12)	5300 (7)	1719 (10)	9003 (6)	55 (9)
C(13)	4496 (7)	1639 (11)	8563 (7)	62 (9)
C(14)	4194 (6)	358 (14)	8277 (7)	69 (9)
C(15)	4688 (8)	−749 (10)	8460 (6)	55 (9)
C(16)	5501 (6)	−578 (12)	8929 (6)	34 (8)
C(17)	6059 (7)	−1770 (10)	9199 (6)	38 (9)
C(18)	5838 (6)	−3115 (13)	8987 (6)	63 (9)
C(19)	6383 (8)	−4155 (11)	9274 (8)	80 (10)
C(20)	7120 (7)	−3846 (12)	9766 (7)	70 (10)
C(21)	7305 (6)	−2481 (12)	9936 (6)	51 (8)
C(22)	8948 (6)	2948 (12)	10524 (7)	58 (9)
C(23)	9743 (7)	3470 (9)	10715 (6)	55 (9)
C(24)	10339 (6)	2972 (11)	10258 (7)	56 (9)
C(25)	10139 (6)	1963 (10)	9620 (6)	45 (8)
C(26)	9323 (7)	1495 (9)	9448 (6)	35 (7)
C(27)	9067 (7)	412 (9)	8755 (6)	37 (8)
C(28)	9601 (5)	−51 (10)	8149 (7)	56 (8)
C(29)	9320 (7)	−1051 (11)	7539 (6)	64 (9)
C(30)	8540 (7)	−1580 (10)	7522 (6)	62 (9)
C(31)	8057 (5)	−1076 (10)	8151 (7)	51 (8)

Table 2. *Atomic positional parameters ($\times 10^4$) and U_{eq} values ($\times 10^3$) for the Ba complex*

$$U_{eq} = \tfrac{1}{2}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ba	0000	854 (1)	2500	51 (1)
N(1)†	235 (7)	1544 (11)	776 (7)	66 (8)
N(3)	1838 (7)	357 (11)	3311 (9)	61 (9)
N(4)	1323 (7)	2851 (11)	3416 (9)	64 (9)
C(8)	229 (8)	1683 (13)	−49 (10)	42 (9)
S(9)	217 (2)	1965 (4)	−1177 (2)	65 (3)
C(12)	2083 (9)	−900 (15)	3292 (11)	72 (12)
C(13)	2957 (9)	−1286 (13)	3563 (11)	66 (11)
C(14)	3576 (8)	−350 (16)	3828 (12)	71 (12)
C(15)	3326 (9)	963 (14)	3835 (12)	67 (10)
C(16)	2463 (9)	1270 (14)	3598 (10)	51 (11)
C(17)	2204 (10)	2680 (14)	3710 (10)	55 (11)
C(18)	2826 (9)	3717 (14)	4063 (12)	69 (11)
C(19)	2554 (10)	4948 (14)	4142 (12)	74 (12)
C(20)	1655 (10)	5161 (14)	3851 (11)	68 (11)
C(21)	1117 (9)	4103 (16)	3528 (11)	67 (11)

† N(2), N(5), and N(6) are related to N(1), N(3) and N(4) by symmetry.

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

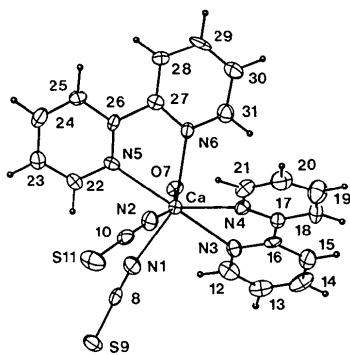|	Ca complex	Ba complex		Ca complex	Ba complex		Ca complex	Ba complex
M–N(1)	2.400(8)	2.77(1)	N(1)–M–N(2)	85.0(2)	150.8(3)	C(12)–C(13)–C(14)	117(1)	118(1)
M–N(2)	2.478(6)	–	N(1)–M–N(3)	86.2(3)	80.7(3)	C(13)–C(14)–C(15)	119(1)	118(1)
M–N(3)	2.540(7)	2.86(1)	N(1)–M–N(4)	129.5(3)	80.5(3)	C(14)–C(15)–C(16)	119(1)	120(1)
M–N(4)	2.520(8)	2.87(1)	N(1)–M–N(5)	88.4(3)	104.5(3)	N(3)–C(16)–C(15)	121.3(9)	122(1)
M–N(5)	2.506(8)	–	N(1)–M–N(6)	150.7(3)	79.1(4)	N(3)–C(16)–C(17)	116.9(8)	116(1)
M–N(6)	2.559(8)	–	N(1)–M–O(7)	87.2(2)	–	C(15)–C(16)–C(17)	121(1)	120(1)
M–O(7)	2.432(5)	–	N(1)–M–S(11')	–	134.2(2)	C(16)–C(17)–C(18)	123.6(9)	121(1)
M–S(9')	–	3.357(9)	N(2)–M–N(3)	123.3(3)	–	C(16)–C(17)–N(4)	114.9(9)	114(1)
N(1)–C(8)	1.138(12)	1.19(2)	N(2)–M–N(4)	80.0(2)	–	C(18)–C(17)–N(4)	121.5(9)	123(1)
C(8)–S(9)	1.656(9)	1.64(1)	N(2)–M–N(5)	77.9(2)	–	C(17)–C(18)–C(19)	119.9(9)	119(1)
N(2)–C(10)	1.146(9)	–	N(2)–M–N(6)	98.0(2)	–	C(18)–C(19)–C(20)	119(1)	118(1)
C(10)–S(11)	1.604(8)	–	N(2)–M–O(7)	159.7(2)	–	C(19)–C(20)–C(21)	118(1)	117(1)
N(3)–C(12)	1.322(14)	1.34(1)	N(2)–M–S(11')	–	74.4(2)	N(4)–C(21)–C(20)	124.1(9)	127(1)
N(3)–C(16)	1.345(14)	1.33(1)	N(3)–M–N(4)	63.8(3)	56.2(3)	M–N(4)–C(17)	122.2(6)	125.2(9)
C(12)–C(13)	1.385(16)	1.42(2)	N(3)–M–N(5)	157.9(3)	159.7(3)	M–N(4)–C(21)	119.5(4)	121.7(9)
C(13)–C(14)	1.400(15)	1.34(2)	N(3)–M–N(6)	115.0(2)	143.5(4)	C(17)–N(4)–C(21)	117.5(8)	112(1)
C(14)–C(15)	1.361(17)	1.40(2)	N(3)–M–O(7)	74.8(2)	–	M–N(5)–C(22)	119.6(7)	–
C(15)–C(16)	1.422(15)	1.39(2)	N(3)–M–S(11')	–	81.4(2)	M–N(5)–C(26)	122.2(6)	–
C(16)–C(17)	1.508(15)	1.52(2)	N(4)–M–N(5)	133.7(3)	–	C(22)–N(5)–C(26)	117.7(8)	–
C(17)–N(4)	1.324(13)	1.38(2)	N(4)–M–N(6)	79.5(3)	90.5(3)	N(5)–C(22)–C(23)	123.6(9)	–
C(17)–C(18)	1.398(16)	1.41(2)	N(4)–M–O(7)	119.0(2)	–	C(22)–C(23)–C(24)	118.7(9)	–
C(18)–C(19)	1.387(16)	1.35(2)	N(4)–M–S(11')	–	118.3(2)	C(23)–C(24)–C(25)	119.1(9)	–
C(19)–C(20)	1.352(16)	1.41(2)	N(5)–M–N(6)	64.1(3)	–	C(24)–C(25)–C(26)	119.5(9)	–
C(20)–C(21)	1.393(16)	1.35(2)	N(5)–M–O(7)	83.1(2)	–	N(5)–C(26)–C(25)	121.4(8)	–
N(4)–C(21)	1.347(13)	1.34(2)	N(5)–M–S(11')	–	81.6(2)	N(5)–C(26)–C(27)	116.7(9)	–
N(5)–C(22)	1.332(12)	–	N(6)–M–O(7)	80.0(2)	–	C(25)–C(26)–C(27)	121.9(9)	–
N(5)–C(26)	1.340(13)	–	N(6)–M–S(11')	–	136.3(2)	C(26)–C(27)–C(28)	121.8(9)	–
C(22)–C(23)	1.390(15)	–	S(11')–M–S(9')	–	63.5(2)	N(6)–C(27)–C(26)	115.6(9)	–
C(23)–C(24)	1.351(16)	–	M–N(1)–C(8)	170.1(7)	169.9(8)	C(28)–C(27)–N(6)	122.6(8)	–
C(24)–C(25)	1.378(14)	–	N(1)–C(8)–S(9)	177.9(9)	176(1)	C(27)–C(28)–C(29)	118.1(1)	–
C(25)–C(26)	1.400(15)	–	M–N(2)–C(10)	146.3(7)	–	C(28)–C(29)–C(30)	120(1)	–
C(26)–C(27)	1.499(12)	–	N(2)–C(10)–S(11)	178.1(9)	–	C(29)–C(30)–C(31)	117.4(9)	–
N(6)–C(27)	1.347(13)	–	M–N(3)–C(12)	121.5(7)	116.9(8)	N(6)–C(31)–C(30)	124.2(9)	–
C(27)–C(28)	1.409(14)	–	M–N(3)–C(16)	119.4(6)	125.8(9)	M–N(6)–C(27)	120.7(6)	–
C(28)–C(29)	1.372(14)	–	C(12)–N(3)–C(16)	118.2(8)	116(1)	M–N(6)–C(31)	122.0(6)	–
C(29)–C(30)	1.373(16)	–	N(3)–C(12)–C(13)	124(1)	123(1)	C(27)–N(6)–C(31)	116.9(8)	–
C(30)–C(31)	1.393(14)	–						
N(6)–C(31)	1.345(12)	–						

Fig. 1. *ORTEP* drawing of the Ca complex. The thermal ellipsoids are drawn at the 35% probability level.
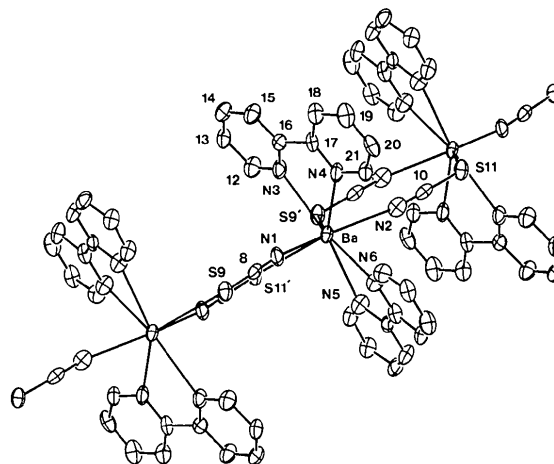
Fig. 2. *ORTEP* drawing of the Ba complex. The thermal ellipsoids are drawn at the 35% probability level.

Fig. 2 is an *ORTEP* drawing of the Ba complex showing the thiocyanate groups bridging the Ba²⁺ ions. The Ba²⁺ ion is eight-coordinate and the geometry around the ion is best described as a distorted square antiprism. The idealized hard-sphere model gives two δ values of 0.0° and eight of 52.4° (Muetterties & Guggenberger, 1974). The Ba complex has two values of 7.4° and eight values which vary from 41.0 to 80.1° with the average being 51.3°. The two Ba–S distances of 3.357 (9) Å are considerably longer than the six Ba–N distances which average 2.83 (2) Å. The preference in coordination of the thiocyanate ion *via* the N atom is supported by the observation of a very weak Ba–S interaction.

The coordination sphere of the Ca complex is completed by a water of hydration; however, the anhydrous Ba complex fills its coordination sphere through weak interactions with thiocyanate S atoms from an adjacent complex. It is reasonable to expect that an anhydrous Ca complex might contain bridging thiocyanate groups; however, the relative sizes of the Ba²⁺ and Ca²⁺ ions influence the coordination number and geometry.

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Tris(3-hydroxy-4*H*-pyran-4-onato)iron(III), C₁₅H₉FeO₉

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Abstract. $M_r = 389 \cdot 08$, rhombohedral, $R\bar{3}c$, $a = 11 \cdot 722$ (1) Å, $\alpha = 47 \cdot 77$ (1)°, $U = 808 \cdot 6$ Å³, $Z = 2$, $D_x = 1 \cdot 598$, $D_m = 1 \cdot 59$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 801$ mm⁻¹, $F(000) = 394$, $T = 293$ (1) K. Final $R = 0 \cdot 021$ for 746 observed diffractometer data. The molecule has exact C_3 symmetry with distorted octahedral coordination of the Fe atom.

Introduction. Recently we reported structural details of both a monomeric and a dimeric complex of iron(III) with 1,2-benzenediol (pyrocatechol) (Anderson, Buckingham, Robertson & Webb, 1982; Anderson, Webb, Buckingham & Robertson, 1982). Comparison of the chemical and spectroscopic properties of these compounds with those of the iron(III) enterochelin trianion permitted the identification of [FeO₆] rather than [FeO₃N₃] at the iron(III) coordination site in the siderophore (Anderson, Buckingham, Robertson, Webb, Murray & Clark, 1976). However, e.p.r. and Mössbauer data for both the pyrocatechol complexes

and the siderophores have resisted complete explanation, particularly as regards the symmetry of the coordination site relative to that of the spin Hamiltonian required to reproduce the spectral splitting (Oosterhuis & Spartalian, 1974; Oosterhuis, 1974). Unlike both the siderophore and the pyrocatechol complexes the title complex is uncharged, and might be expected to exhibit strict trigonal symmetry and be devoid of intermolecular hydrogen bonding.

Experimental. Prepared from 3-hydroxy-4-pyrone (pyromeconic acid) and basic ferric acetate by method of Garkusha (1946), recrystallized from dimethyl sulfoxide as small crimson rhombs, D_m measured by flotation, crystal used for data collection had dimensions $0 \cdot 20 \times 0 \cdot 18 \times 0 \cdot 15$ mm parallel to **a***, **b*** and **c*** respectively; reflection intensities for one complete reciprocal-space hemisphere ($3 < 2\theta < 50°$) recorded on a Picker FACS-1 diffractometer, θ–2θ scan mode, scan velocity 2° min⁻¹ (2θ), two 10s background counts at extremes, Mo $K\bar{\alpha}$, graphite-crystal monochromator, 2880 reflections excluding standards; quoted cell dimensions and standard errors derived from least-squares analysis of setting angles for 12 well centered reflections with $39 < 2\theta < 45$ (Mo $K\alpha_1$ radiation); intensities of three standard reflections (088, 808 and 880) did not vary significantly during data

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