

Structure of Diaquabis(4-methyl-*N*-8-quinolylbenzenesulphonamido-*N,N'*)cobalt(II)–Acetone (1/1), $[\text{Co}(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2\text{S})_2(\text{H}_2\text{O})_2]\cdot\text{C}_3\text{H}_6\text{O}$

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Abstract. $M_r = 747.75$, monoclinic, $P2_1/c$, $a = 13.555$ (4), $b = 10.519$ (2), $c = 24.469$ (8) Å, $\beta = 101.07$ (3)°, $V = 3424$ (2) Å³, $Z = 4$, $D_x = 1.45$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.70$ mm⁻¹, $F(000) = 1566$, room temperature, final $R = 0.048$ for 2833 observed reflections. The Co atom, which has a distorted octahedral coordination, is bonded to the N atoms of the chelating agent and two water molecules that have been retained in the Co coordination sphere in the organic phase after the extraction process. The bonding to Co causes changes in geometry around the amido N(11) atom compared with the free molecule.

Introduction. In our studies on metal extraction equilibria we have recently reported the structure of 4-methyl-*N*-8-quinolylbenzenesulphonamide (Germain, Declercq, Castresana, Elizalde & Arrieta, 1983), a chelating agent with a similar formula to the active component in LIX 34, a commercial chelating agent which has been used in industrial solvent-extraction processes to recover Cu^{II} (Kordosky, 1976). Here we present the structure of its Co^{II} complex.

Experimental. A Co(NO₃)₂ aqueous solution was shaken with an excess of 4-methyl-*N*-8-quinolylbenzenesulphonamide in toluene; powdery red precipitate obtained in the organic phase; after filtering, washing with toluene and acetone, complex was recrystallized from acetone; bright red hexagonal prismatic crystals, crystal ca 0.15 × 0.10 × 0.03 mm, cell parameters by least squares from the setting angles of 15 reflections; 5068 independent reflections measured with Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scans up to $2\theta = 47^\circ$; 1 standard reflection measured every 50 reflections showed only random deviation from its mean intensity; Lorentz and polarization but not absorption corrections; 2833 reflections [$I \geq 2.5\sigma(I)$]

considered observed and included in the refinement; index range $h -15-14$, $k 0-11$, $l 0-27$; coordinates of Co obtained from sharpened Patterson synthesis; remaining non-H atoms determined with *DIRDIF80* (Beurskens, Bosman, Doesburg, Gould, van den Hark & Prick, 1980); least-squares refinement with *SHELX76* (Sheldrick, 1976), $\sum w(\Delta F)^2$ minimized, anisotropic thermal parameters for non-H atoms; H positions determined by difference Fourier synthesis, refined with an overall isotropic temperature factor; final R and R_w 0.048 and 0.043, $w = [\sigma^2(F) + 0.00025F^2]^{-1}$; scattering factors from *International Tables for X-ray Crystallography* (1974), max. and min. electron densities in final difference map ± 0.30 e Å⁻³, max. Δ/σ (for non-H atoms) = 1.55.

Discussion. Table 1† gives the final atomic parameters with their B_{eq} values (Willis & Pryor, 1975) following the numbering shown in Fig. 1 (Motherwell & Clegg, 1978).

As can be seen from Figs. 2 and 3, the bond distances and angles of the two LIX 34 ligands are very similar. The isoquinoline groups are planar within experimental error, the largest atomic deviation from the mean plane for each molecule being 0.04 (1) Å [C(8A)] and 0.06 (2) Å [C(3B)]. They are almost perpendicular with a dihedral angle of 82 (1.5)°. The phenyl groups are also planar, the largest deviation from their respective mean planes being 0.004 (2) Å [C(18A)] and 0.014 (1) Å [C(17B)]. Table 2 gives the bond angles around the central Co atom illustrating its distorted octahedral coordination. The chelating effect of the reagent is caused by the two N atoms. This produces a change in the surroundings of the basic N(11) atom; the angle S(12)–N(11)–C(9) is reduced

† 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 39165 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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from 127–125 (1)° for molecules *A* and *B* in 4-methyl-*N*-8-quinolylbenzenesulphonamide (Germain *et al.*, 1983) to 119–120 (1)° in this complex and angles O(13)–S(12)–N(11) and N(11)–C(9)–C(8) are increased from 105–108 (1) and 123–125 (1)° to 114 (1) and 127–128 (1)°. The bond distances and angles for the acetone molecule which crystallizes with the complex are listed in Table 2.

Table 1. Fractional atomic coordinates ($\times 10^4$; for Co $\times 10^5$) with e.s.d.'s in parentheses and B_{eq} values (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Co	71590 (10)	38540 (10)	80084 (5)	2.65
N(1A)	7384 (3)	1992 (4)	8348 (2)	2.73
C(2A)	7112 (5)	912 (5)	8080 (3)	3.15
C(3A)	7359 (5)	-280 (6)	8320 (3)	3.44
C(4A)	7910 (5)	-357 (6)	8839 (3)	3.31
C(5A)	8232 (4)	760 (5)	9133 (3)	2.85
C(6A)	8834 (5)	755 (6)	9678 (3)	3.76
C(7A)	9156 (5)	1878 (7)	9922 (3)	4.12
C(8A)	8899 (4)	3056 (6)	9667 (3)	3.05
C(9A)	8281 (4)	3121 (5)	9147 (2)	2.43
C(10A)	7965 (4)	1940 (5)	8873 (2)	2.40
N(11A)	7935 (3)	4227 (4)	8849 (2)	2.83
S(12A)	8242 (2)	5579 (2)	9116 (1)	3.85
O(13A)	9323 (3)	5762 (4)	9276 (2)	5.25
O(14A)	7706 (4)	6506 (4)	8737 (2)	6.05
C(15A)	7760 (5)	5733 (5)	9740 (2)	2.84
C(16A)	6741 (5)	5553 (7)	9736 (3)	4.70
C(17A)	6395 (6)	5697 (7)	10232 (4)	5.47
C(18A)	7003 (5)	6001 (6)	10718 (3)	3.95
C(19A)	8008 (5)	6163 (6)	10717 (3)	4.07
C(20A)	8389 (5)	6036 (6)	10235 (3)	3.33
C(21A)	6620 (7)	6119 (9)	11244 (4)	6.54
N(1B)	8473 (4)	3657 (5)	7669 (2)	3.04
C(2B)	9394 (5)	4036 (8)	7916 (3)	4.44
C(3B)	10239 (6)	3816 (10)	7671 (4)	5.73
C(4B)	10121 (7)	3183 (9)	7183 (4)	5.49
C(5B)	9155 (5)	2801 (6)	6900 (3)	3.90
C(6B)	8979 (7)	2211 (7)	6369 (3)	4.66
C(7B)	8025 (7)	1975 (7)	6106 (3)	4.72
C(8B)	7195 (6)	2236 (6)	6356 (3)	3.84
C(9B)	7317 (5)	2778 (6)	6883 (3)	2.87
C(10B)	8332 (5)	3079 (6)	7159 (3)	2.97
N(11B)	6572 (3)	3079 (4)	7194 (2)	2.66
S(12B)	5420 (1)	2796 (2)	6932 (1)	3.11
O(13B)	5255 (3)	1562 (4)	6667 (2)	3.88
O(14B)	4852 (3)	3023 (4)	7370 (2)	3.88
C(15B)	5012 (4)	3950 (6)	6412 (3)	3.01
C(16B)	4556 (5)	3595 (7)	5880 (3)	4.13
C(17B)	4206 (6)	4530 (9)	5489 (3)	4.92
C(18B)	4269 (5)	5802 (7)	5623 (3)	4.28
C(19B)	4727 (5)	6128 (8)	6163 (3)	4.32
C(20B)	5106 (5)	5234 (7)	6554 (3)	3.74
C(21B)	3866 (7)	6821 (10)	5212 (5)	6.58
O(1W)	5775 (3)	4231 (4)	8268 (2)	3.74
O(2W)	7016 (4)	5760 (4)	7682 (2)	3.94
C(1K)*	1531 (6)	4062 (7)	3532 (4)	4.75
C(2K)*	2319 (9)	4483 (10)	4001 (5)	7.38
C(3K)*	493 (8)	4000 (10)	3644 (5)	7.54
O(4K)*	1706 (4)	3761 (5)	3089 (2)	6.82

* Atoms of the acetone molecule.

Table 2. Bond angles (°) at Co and at S, and dimensions (\AA , °) of the acetone molecule

N(1A)–Co–N(11A)	77.7 (2)	N(1A)–Co–O(2W)	176.9 (2)
N(1B)–Co–N(11A)	89.7 (2)	N(11A)–Co–O(2W)	100.2 (2)
N(1B)–Co–N(11A)	95.7 (2)	N(1B)–Co–O(2W)	88.2 (2)
N(11B)–Co–N(11A)	90.7 (2)	N(11B)–Co–O(2W)	91.1 (2)
N(11B)–Co–N(11A)	166.9 (2)	O(1W)–Co–O(2W)	85.2 (2)
N(11B)–Co–N(1B)	77.9 (2)	C(15A)–S(12A)–N(11A)	108.9 (3)
O(1W)–Co–N(1A)	97.1 (2)	O(14A)–S(12A)–O(13A)	116.1 (3)
O(1W)–Co–N(11A)	88.7 (2)	O(13B)–S(12B)–O(14B)	114.7 (3)
O(1W)–Co–N(1B)	172.6 (2)	C(15B)–S(12B)–N(11B)	107.9 (3)
O(1W)–Co–N(11B)	99.0 (2)		
C(2K)–C(1K)	1.48 (2)	C(3K)–C(1K)–C(2K)	116 (1)
C(3K)–C(1K)	1.49 (2)	O(4K)–C(1K)–C(2K)	123 (1)
O(4K)–C(1K)	1.20 (2)	O(4K)–C(1K)–C(3K)	121 (1)

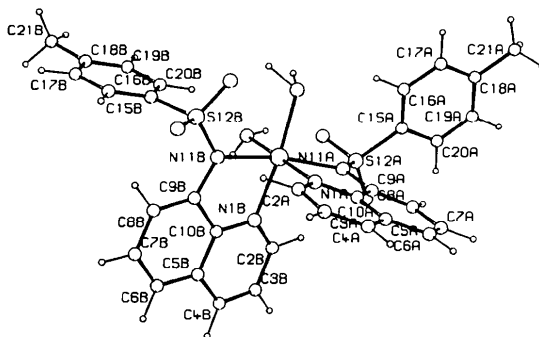


Fig. 1. View of the molecule drawn with PLUTO (Motherwell & Clegg, 1978).

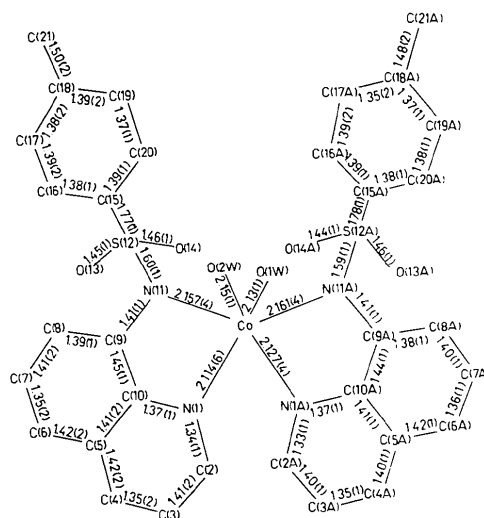


Fig. 2. Bond distances (\AA) with e.s.d.'s in parentheses.

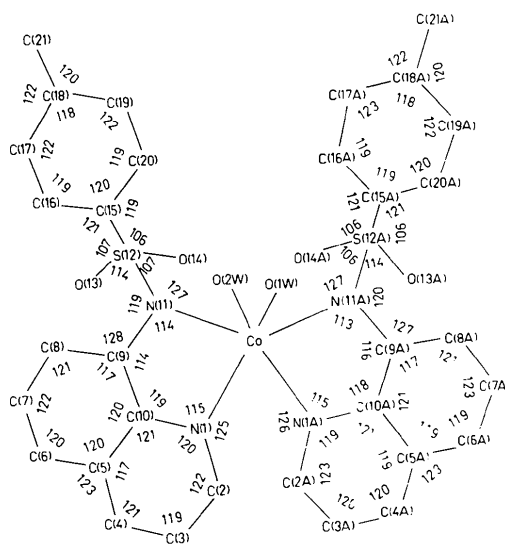


Fig. 3. Bond angles (°); e.s.d.'s $< 1^\circ$.

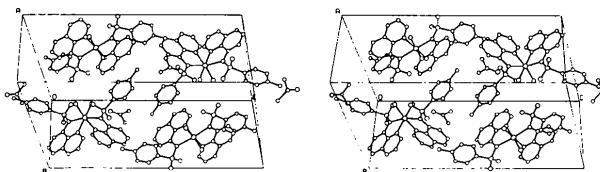


Fig. 4. Stereoscopic view of the molecular packing. Origin left top front corner, **a** into paper, **b** vertically downwards, **c** horizontally to the right.

The molecular packing is shown in Fig. 4.

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Bis(succinimido-*N,N'*)argentate(I) de Sodium Pentahydraté, Na[Ag(C₄H₄NO₂)₂].5H₂O

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Abstract. $M_r = 417.1$, orthorhombic, $Cmc2_1$, $a = 6.856$ (5), $b = 21.74$ (1), $c = 20.589$ (6) Å, $V = 3068$ Å³, $Z = 8$, $D_m = 1.80$ (3), $D_x = 1.81$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.37$ mm⁻¹, $F(000) = 1792$, 294 (1) K, $R = 0.030$ for 1704 independent reflections. The structure consists of [Ag(C₄H₄NO₂)₂]⁻ and Na⁺ ions and water molecules. It is mainly made up of plane sheets at $x = 0$ and $x = \frac{1}{2}$. The Ag atom is twofold coordinated and the Ag–N bonds seem strongly covalent. Interatomic distances indicate there is an unlocated orbital in which the O–C–N–C–O chain is involved. The coordination polyhedron of the Na⁺ ions is either a slightly distorted octahedron or a bipyramid with a trigonal base constituted of O atoms.

Introduction. Le point de départ de ce travail est la recherche d'une méthode de dosage des bases puriques. Ces composés sont amphotères et présentent, dans les solvants non aqueux courants, des propriétés acido-basiques très faibles. Aussi, a-t-on envisagé de les titrer en formant leurs dérivés argentiques (Leroux, 1969). L'étude de ces dérivés par diffraction X a été entreprise

dans le but de déterminer leur structure moléculaire que les spectrométries IR et de RMN ¹H n'ont pas permis de connaître avec certitude. Toutefois, il n'a pas été possible jusqu'ici d'obtenir des monocristaux des composés de la théophylline ou de la théobromine de taille suffisante pour réaliser une étude structurale. C'est la raison pour laquelle nous avons préparé un dérivé du succinimide. Celui-ci contient, comme les bases puriques, le groupement O–C–N–C–O et donne un dérivé d'argent(I) qui cristallise facilement.

Partie expérimentale. 0,5 mmol dm⁻³ de succinimide en solution 0,01 mol dm⁻³ + 1 mmol dm⁻³ NaOH + 0,25 mmol dm⁻³ AgNO₃. Evaporation sous vide à 333 K de la solution ramenée à pH = 9. Aiguilles incolores. D_m par méthode du flacon. Cristal choisi: prisme à bases parallélogrammes, 0,22 × 0,25 × 0,30 mm. Diffractomètre automatique Enraf–Nonius CAD-4. Dimensions de la maille calculées avec 15 réflexions telles que $8,90 \leq \theta \leq 20,15^\circ$. Max. $(\sin \theta)/\lambda$ 0,661 Å⁻¹, $0 \leq h \leq 9$, $0 \leq k \leq 28$, $0 \leq l \leq 27$. Réflexions standards: 117, 2,10,4 et 0,0,12. Diminution d'environ