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Base-induced Conversion of Macrocyclic Tetradentate to Bidentate Salicylamide Complexes. Structure of the Picoline Adduct to a Co^{II}(1,2-bis(*o*-hydroxybenzoyl)ethylenediamine)

J. D. KOOLA and J. K. KOCHI

Department of Chemistry, University of Houston, University Park, Houston, Tex. 77004, U.S.A.

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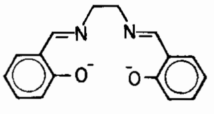
Abstract

The synthesis of the cobalt(II) complex of the tetradentate ligand 1,2-bis(*o*-hydroxybenzoyl)ethylenediamine (salam) and its 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethyl analogue (**I**) is described. Treatment of **I** with picoline yields the base adduct **II** showing an unusual octahedral coordination of cobalt(II) to only a single salicyl group (as a η^2-β-ketoenolate ligand) and four picoline bases. The remainder of the original tetradentate ligand exists as a pendant salicylamide moiety that is stabilized by two very strong hydrogen bonds. The structural transformation of **I** attendant upon the addition of pyridine bases is discussed. Complex **II** crystallized in the monoclinic space group $P2_1/c$ with lattice constants $a = 12.174(4)$, $b = 10.430(6)$, $c = 40.790(24)$ Å, $\beta = 98.16(4)°$ and $Z = 4$.

Introduction

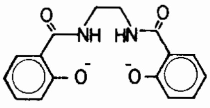
Schiff base complexes have occupied a central role in the development of the coordination chemistry of transition metals such as cobalt [1, 2]. Among these, the bis-Schiff base ligand salenH_2 has been especially useful owing to the presence of two pairs of imino nitrogen and phenolic oxygen atoms that form a square-planar array of chelating atoms for effective metal coordination [3–6], *i.e.*



salen

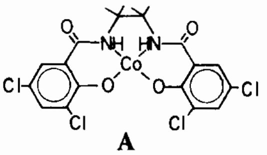
Such an open macrocyclic ligand structure also offers a degree of flexibility that is not present in the more commonly used porphyrin and phthalocyanin systems [2, 7]. Furthermore the direct condensation of the readily available salicylaldehydes and diamines allows a wide variety of substituted salen^{2-} ligands and analogues to be readily synthesized [1, 8].

Our interest in salen metal complexes derives from their use as oxidation catalysts, as in the recently isolated cationic oxochromium complex O=Cr(salen)$^+$ [9]. However the unsaturated linkage (>C=N–) in salen presents a point of ligand vulnerability that is sufficient to limit catalyst stability, especially under severe oxidative conditions [10, 11]. In order to preserve the tetradentate N_2O_2-ligation intact, we turned to the oxidatively more stable amide analogues [12, 13] – the closest relative to salen^{2-} being the bis-salicylamide (salam), *viz.*



salam

Indeed we have found the cobalt(II) complex of 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethylsalam to be an effective catalyst for the epoxidation of various olefins [14]. We infer from the spectroscopic and elemental analyses (see 'Experimental') that Co^{II}(Cl_4Me_4(salam) (**I**) is the expected coordination complex **A**.



A

Unfortunately we were unable to grow a single crystal of this cobalt(II) complex to establish its structure by X-ray crystallography. However, it could be converted to the 4-picoline adduct (**II**) that was successfully isolated as a single crystal and the unusual coordination elucidated, as described in this report.

Experimental

Materials

Cobaltous acetate $Co(O_2CCH_3)_2 \cdot 4H_2O$ (Matheson, Coleman and Bell), salicylic acid (Aldrich), acetylsalicylic acid (Fisher) and ethylenediame (Aldrich) were used as received. Pyridine and 4-picoline

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(Aldrich) were refluxed over calcium hydride and distilled under an argon atmosphere prior to use. 2,3-Diamino-2,3-dimethylbutane was prepared from 2,3-dinitro-2,3-dimethylbutane by acidic reduction with granular tin, followed by distillation from KOH pellets [15].

Acetyl-3,5-dichlorosalicylic acid was prepared by passing chlorine through an acetic acid solution of salicylic acid, followed by acetylation with acetic anhydride. It was converted to the acid chloride with thionyl chloride in the presence of a catalytic amount of anhydrous $AlCl_3$ at 50–60 °C. The acid chloride was treated with 2,3-dimethyl-2,3-diaminobutane in dichloromethane and then triethylamine. Work-up yielded a colorless solid which was recrystallized from aqueous acetone followed by removal of acetone *in vacuo*. Melting point (m.p.) 198–200 °C. Yield: 77% of 2,2,4,4′-tetrachloro-8,8,8′,8′-tetramethyl-salamH_2 [2,3-bis(3,5-dichloro-2-hydroxybenzamido)-2,3-dimethylbutane]. ^1H NMR ($CDCl_3$): δ 1.59 (s, 12H); 7.44 (d, $J = 2Hz$, 2H); 7.56 (d, $J = 2Hz$, 2H); 7.95 (s, 2H); 12.18 (s, 2H). IR (KBr): 3374(m), 3269(m), 3086(w), 2995(m), 1644(vs), 1589(vs), 1562(vs), 1548(vs, br), 1450(vs, br), 1400(w), 1360(vs), 1330(vs), 1253(vs), 1204(w), 1190(w), 1144(s), 977(w), 930(m), 879(s), 859(m), 791(s), 772(m), 753(m), 736(s), 709(w), 687(w), 632(w), 610(w), 561(m), 520(m), 485(m).

Synthesis of $Co^{II}(Cl_4Me_4salam)$ (I)

A solution containing $Co(OAc)_2 \cdot 4H_2O$ (0.125 g, 0.50 mmol) and 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethylsalamH_2 (0.25 g, 0.51 mmol) in methanol was deaerated with a stream of argon and then refluxed for 3 h, during the course of which a light purple solid separated. Alternatively a solution of $Cl_4Me_4salamH_2$ (8.0 g, 16.2 mm) in 1000 ml of deoxygenated methanol was refluxed under an argon atmosphere. To this was slowly added a solution of cobaltous acetate [$Co(OAc)_2 \cdot 4H_2O$, 4.3 g, 17.3 mmol] in 300 ml methanol and the mixture stirred overnight at 25 °C. The solution was filtered to remove particulate matter, and the clear filtrate carefully concentrated to yield a purple solid. Yield 8.0 g (89%) of $Co(Cl_4Me_4salam) \cdot 3/2H_2O$. *Anal.* Calc. for $C_{20}H_{18}Cl_4N_2O_4Co \cdot 3/2H_2O$: C, 41.55; 3.66; N, 4.85. Found: C, 41.46; H, 3.75; N, 4.80%. IR(KBr): 3230(m, br), 3085(m), 2995(m), 1620(vs, br), 1568(vs, br), 1447(vs, br), 1403(s), 1379(w), 1343(m), 1313(w), 1294(w), 1250(s), 1234(s), 1138(s), 1097(w), 1026(w), 1001(vw), 980(w), 930(w), 873(s), 794(s), 764(s), 711(m), 676(m), 643(w), 613(w), 559(w), 534(m), 479(w), 457(w), 419(m).

The light purple sesquihydrate when dried over P_2O_5 in vacuum yielded the light blue monohydrate, $Co^{II}(Cl_4Me_4salam)H_2O$. *Anal.* Calc. for $C_{20}H_{18}Cl_4CoN_2O_4 \cdot H_2O$: C, 42.21; H, 3.54. Found: C, 42.35; H, 3.70%.

The cobalt(II) complex **I** was very stable to air either in the solid state or when suspended in solvents. All attempts to crystallize **I** were unsuccessful owing to its insolubility in organic solvents except pyridines. Various attempts were made to obtain the complex in a crystalline form before its precipitation. The following methods were followed. The complex was prepared in solution in methanol at high dilution and carefully concentrated taking care not to precipitate the complex. Then, solvents like ether, pentane, hexane or dichloromethane were slowly allowed to diffuse into the complex solution in methanol at room temperature or ice bath temperature. Nevertheless, a non-crystalline material precipitated. Attempts to crystallize the complex by carrying out the synthesis in a biphasic system (water and benzene) using a phase-transfer catalyst or by solvent extraction of the ligand into aqueous methanolic solution of $Co(OAc)_2 \cdot 4H_2O$ were also not successful.

Synthesis of $Co(Cl_4Me_4salam)(picoline)_4$

Complex **I** could be crystallized as the 4-picoline adduct. Typically a solution of **I** (1 g in 1 ml) in 4-picoline was prepared by stirring for ~2 h. Hexane was then allowed to diffuse slowly into the 4-picoline solution. Over a period of 24 h crystallization began. After 48 h 80% of the complex was recovered as highly crystalline 4-picoline adduct for X-ray crystallography (*vide infra*). IR(KBr): 3428(w, br), 3222(w, br), 3072(w), 2990(w), 1620(vs, br), 1562(vs, br), 1447(vs, br), 1398(m), 1379(m), 1341(m), 1313(m), 1250(s), 1229(s), 1212(s), 1136(s), 1018(s), 873(s), 813(s), 794(s), 761(s), 725(m), 676(m), 537(m), 493(s), 419(m).

The red–orange 4-picoline adduct dissolved in dry dichloromethane to give a light-blue solution. A gas chromatographic analysis of the solution indicated that 4 molecules of 4-picoline were liberated from the complex on dissolution. On adding excess 4-picoline to the light blue dichloromethane solution, the color turned to orange–yellow. When $CHCl_3$ was added to the 4-picoline adduct, a light-blue–grey solid was immediately formed. The IR spectrum of this solid resembled the IR spectrum of the red–orange 4-picoline adduct. Both showed a characteristic strong absorption at 493 cm^{-1}. The 4-picoline adduct when exposed to air over a period of time was converted to a light-blue solid with loss of crystalline character. The 4-picoline adduct either in the solid state or in solution in 4-picoline was stable to air.

A finely pulverized powder of **I** (0.5 g) was mounted on an aluminum block and rotated at 4 kHz. The X-radiation with $\lambda = 1.54050$ Å was generated at a fixed voltage of 30 kV and fixed current of 10 mA. Only a nondescript, broad diffraction pattern with a few occasional peaks was observed at low angles with a crude maximum at ~15–30°.

TABLE I. Data Collection and Processing Parameters

Space group	$P2_1/c$, monoclinic
Cell constants	$a = 12.174(4)$ Å
	$b = 10.430(6)$ Å
	$c = 40.790(24)$ Å
	$\beta = 98.16(4)^\circ$
	$V = 5127$ Å^3
Molecular formula	$CoCl_4O_4N_6C_{44}H_{46}\cdot NC_6H_7\cdot H_2O$
Formula weight	1034.8
Formula units per cell	$Z = 4$
Density	$\rho = 1.34$ g cm^{-3}
Absorption coefficient	$\mu = 5.93$ cm^{-1}
Radiation (Mo Kα)	$\lambda = 0.71073$ Å
Collection range	$4^\circ \leqslant 2\theta \leqslant 40^\circ$
Scan width	$\Delta\theta = (0.45 + 0.35 \tan\theta)^\circ$
Maximum scan time	90 s
Scan speed range	0.3 to 5.0 °/min^{-1}
Total data collected	5414
Independent data, $I > 3\sigma(I)$	3445
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.037
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.037
Weights	$w = \sigma(F)^{-2}$

Synthesis of the Pyridine Adduct of I

$Co(OAc)_2\cdot 4H_2O$ (0.125 g, 0.5 mm) dissolved in 20 ml of deaerated methanol was slowly added to a solution of $Cl_4Me_4salenH_2$ (0.25 g, 0.51 mm) in 100 ml deaerated methanol under argon. The solution was kept stirred at 40 °C for 2 h. Pyridine (1 ml) was then added and the mixture stirred overnight. Finally the solvents were removed to obtain a deep blue solid. It was then dissolved in pyridine, and hexane was slowly diffused into this blue solution whereupon the brown pyridine adduct separated. Yield 0.2 g, 57%. IR(KBr): 3234(s, br), 3072(s, br), 2995(m, br), 1657(vs, br), 1573(vs, br), 1447(vs, br), 1379(w), 1343(w), 1308(w), 1250(m), 1220(m), 1141(s), 1097(w), 1070(m), 1040(m), 1013(m), 980(w), 928(w), 873(s), 791(s), 769(s), 701(s), 676(m), 632-(m), 561(m), 529(m), 496(w), 477(w), 449(w), 422(m).

Synthesis of the DMF Adduct of I

The DMF adduct of **I** was prepared by reacting $Co(OAc)_2\cdot 4H_2O$ (0.25 g, 1 mm, dissolved in 20 ml dry DMF) with $Cl_4Me_4salamH_2$ (0.5 g, 1.01 mm, dissolved in 60 ml dry DMF) under argon at 110–120 °C for 3 h. The resulting deep blue solution was dried in vacuum and then washed with benzene and dichloromethane to obtain a blue solid. The blue solid was readily soluble in DMF. However it could not be crystallized from DMF solution. Yield 0.5 g, 71%. IR(KBr): 3085(w), 2995(w), 1622(vs, br), 1554(vs, br), 1442(vs, br), 1343(m), 1316(w), 1250(s), 1144-(s), 1098(w), 1023(w), 980(w), 930(w), 870(m), 835(w), 791(s), 772(m), 734(w), 712(w), 679(s), 668(s), 619(m), 561(w), 537(w), 493(w), 473(w), 452(w), 436(w), 422(w).

Instrumentation

Infrared spectra were recorded on a Nicolet 10 DX FT spectrometer with the aid of potassium bromide pellets. ^1H NMR spectra were obtained on a JEOL FX 90Q FT spectrometer, and all chemical shifts were reported relative to Me_4Si. GC-MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). The X-ray powder diffraction was carried out with a Rigaku Model CN 2005 Miniflex.

X-ray Crystallography of Co(Cl$_4$Me$_4$salam)-(picoline)$_4$

A large, clear red–orange block having approximate dimensions 0.50 × 0.30 × 0.25 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue symmetry was determined to be $2/m$; and from the systematic absences noted the space group was shown unambiguously to be $P2_1/c$. Intensities were measured using the ω scan technique due to the unusually long c axis. The scan rate depended on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In reducing the data, Lorentz and polarization factors were applied, however no correction for absorption was made due to the small absorption coefficient. The structure was

TABLE II. Positional Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	B (Å^2)
Co	0.26324(5)	0.39100(6)	0.37663(1)	3.81(1)
Cl1	0.4461(1)	0.2832(2)	0.48160(3)	6.02(4)
Cl2	0.7812(1)	0.6013(2)	0.46617(3)	7.30(4)
Cl3	0.9823(1)	0.8871(2)	0.44725(4)	8.46(5)
Cl4	0.8682(1)	1.1222(1)	0.33057(3)	5.98(4)
O1	0.3807(2)	0.3202(3)	0.41099(7)	4.08(7)
O2	0.3996(2)	0.4428(3)	0.35250(6)	3.93(7)
O3	0.8044(2)	0.5364(3)	0.36525(7)	4.21(7)
O4	0.8039(2)	0.8653(3)	0.30584(7)	4.60(8)
O5	0.3984(3)	0.5016(4)	0.2101(1)	9.8(2)
N1	0.5782(3)	0.4798(4)	0.34564(7)	3.46(9)
N2	0.7319(3)	0.6343(3)	0.31700(8)	3.57(9)
N3	0.1597(3)	0.4721(4)	0.33323(8)	4.10(9)
N4	0.2546(3)	0.2047(4)	0.35299(8)	3.93(9)
N5	0.2741(3)	0.5813(4)	0.39990(8)	4.10(9)
N6	0.1305(3)	0.3357(4)	0.40464(8)	3.91(9)
N7	0.3879(5)	0.5214(6)	0.1379(1)	7*
C1	0.4707(3)	0.3810(4)	0.42180(9)	3.4(1)
C2	0.5154(3)	0.3761(4)	0.4558(1)	3.8(1)
C3	0.6082(4)	0.4416(5)	0.4693(1)	4.5(1)
C4	0.6650(4)	0.5147(5)	0.4489(1)	4.5(1)
C5	0.6296(3)	0.5193(5)	0.4157(1)	4.1(1)
C6	0.5347(3)	0.4536(4)	0.40137(9)	3.3(1)
C7	0.4997(3)	0.4582(4)	0.3651(1)	3.5(1)
C8	0.5591(3)	0.4995(4)	0.3094(1)	3.7(1)
C9	0.5054(4)	0.3788(5)	0.2921(1)	5.0(1)
C10	0.4823(4)	0.6148(5)	0.3012(1)	4.8(1)
C11	0.6764(3)	0.5258(4)	0.2984(1)	3.8(1)
C12	0.6617(4)	0.5697(5)	0.2619(1)	5.0(1)
C13	0.7491(4)	0.4060(5)	0.3017(1)	5.0(1)
C14	0.7944(3)	0.6327(5)	0.34709(9)	3.6(1)
C15	0.8465(3)	0.7570(4)	0.3582(1)	3.5(1)
C16	0.8914(3)	0.7634(5)	0.3916(1)	4.4(1)
C17	0.9306(4)	0.8777(5)	0.4050(1)	5.0(1)
C18	0.9242(4)	0.9876(5)	0.3865(1)	4.8(1)
C19	0.8809(3)	0.9816(4)	0.3533(1)	4.3(1)
C20	0.8414(3)	0.8671(4)	0.3372(1)	3.7(1)
C21	0.1788(4)	0.4380(5)	0.3032(1)	4.3(1)
C22	0.1273(4)	0.4935(5)	0.2743(1)	4.7(1)
C23	0.0502(4)	0.5904(5)	0.2761(1)	4.8(1)
C24	−0.0070(5)	0.6562(6)	0.2461(1)	7.5(2)
C25	0.0289(3)	0.6246(5)	0.3072(1)	4.3(1)
C26	0.0854(3)	0.5661(5)	0.3347(1)	4.1(1)
C27	0.1617(3)	0.1354(5)	0.3462(1)	4.8(1)
C28	0.1565(4)	0.0207(5)	0.3294(1)	4.9(1)
C29	0.2488(4)	−0.0287(4)	0.3178(1)	4.2(1)
C30	0.2452(4)	−0.1507(5)	0.2986(1)	5.6(1)
C31	0.3453(4)	0.0414(5)	0.3252(1)	4.4(1)
C32	0.3452(3)	0.1532(5)	0.3427(1)	4.5(1)
C33	0.2531(4)	0.6058(5)	0.4301(1)	5.7(1)
C34	0.2639(5)	0.7253(5)	0.4442(1)	6.7(2)
C35	0.2977(4)	0.8268(5)	0.4273(1)	5.9(1)
C36	0.3090(6)	0.9590(6)	0.4412(2)	10.5(2)
C37	0.3213(4)	0.8019(5)	0.3962(1)	5.5(1)
C38	0.3083(4)	0.6809(5)	0.3836(1)	5.2(1)
C39	0.1609(4)	0.2745(5)	0.4330(1)	4.6(1)
C40	0.0893(4)	0.2478(5)	0.4554(1)	4.9(1)
C41	−0.0192(4)	0.2862(5)	0.4492(1)	4.9(1)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C42	−0.0986(4)	0.2593(7)	0.4732(1)	8.6(2)
C43	−0.0519(4)	0.3472(5)	0.4197(1)	5.0(1)
C44	0.0228(4)	0.3705(5)	0.3982(1)	4.6(1)
C45	0.3927(6)	0.4197(8)	0.1238(2)	7*
C46	0.3795(6)	0.3982(8)	0.0917(2)	7*
C47	0.3537(6)	0.5080(8)	0.0696(2)	7*
C48	0.3384(7)	0.488(1)	0.0336(2)	10*
C49	0.3435(6)	0.6174(8)	0.0847(2)	7*
C50	0.3688(6)	0.6170(8)	0.1198(2)	7*
N7′	0.380(1)	0.581(2)	0.1435(4)	7*
C45′	0.403(2)	0.441(2)	0.1391(5)	7*
C46′	0.401(2)	0.362(2)	0.1113(5)	7*
C47′	0.372(2)	0.469(2)	0.0778(5)	7*
C48′	0.378(2)	0.411(3)	0.0620(7)	10*
C49′	0.374(2)	0.593(2)	0.0849(5)	7*
C50′	0.349(2)	0.655(2)	0.1115(5)	7*
H(W)A	0.4160	0.4160	0.2031	4*
H(W)B	0.3593	0.5546	0.2207	4*
H1	0.6660	0.4707	0.3593	4*
H2	0.7500	0.7207	0.3046	4*
H3	0.6337	0.4368	0.4926	6*
H5	0.6702	0.5695	0.4018	6*
H9A	0.5543	0.3077	0.2972	6*
H9C	0.4936	0.3918	0.2689	6*
H9B	0.4375	0.3624	0.2999	6*
H10C	0.4140	0.5979	0.3090	6*
H10B	0.4701	0.6272	0.2780	6*
H10A	0.5159	0.6885	0.3118	6*
H12B	0.7326	0.5873	0.2558	6*
H12A	0.6173	0.6442	0.2596	6*
H12C	0.6271	0.5028	0.2486	6*
H13B	0.7141	0.3402	0.2880	6*
H13C	0.8196	0.4247	0.2952	6*
H13A	0.7596	0.3783	0.3242	6*
H16	0.8965	0.6876	0.4047	6*
H18	0.9506	1.0660	0.3963	6*
H21	0.2320	0.3717	0.3014	6*
H22	0.1441	0.4663	0.2532	6*
H24B	−0.0559	0.5956	0.2309	6*
H24C	0.0442	0.7006	0.2328	6*
H24A	−0.0559	0.7204	0.2546	6*
H25	−0.0252	0.6886	0.3094	6*
H26	0.0705	0.5934	0.3561	6*
H27	0.0963	0.1656	0.3534	6*
H28	0.0880	−0.0248	0.3257	6*
H30C	0.1873	−0.1422	0.2779	6*
H30A	0.2225	−0.2205	0.3124	6*
H30B	0.3181	−0.1684	0.2916	6*
H31	0.4116	0.0100	0.3185	6*
H32	0.4130	0.1965	0.3480	6*
H33	0.2311	0.5368	0.4431	6*
H34	0.2444	0.7381	0.4659	6*
H36C	0.2331	0.9833	0.4468	6*
H36A	0.3344	1.0211	0.4260	6*
H36B	0.3614	0.9532	0.4625	6*
H37	0.3462	0.8685	0.3834	6*
H38	0.3252	0.6657	0.3618	6*
H39	0.2364	0.2464	0.4385	6*

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
H40	0.1154	0.2028	0.4753	6*
H42C	−0.0894	0.1688	0.4808	6*
H42A	−0.1732	0.2777	0.4628	6*
H42B	−0.0776	0.3177	0.4932	6*
H43	−0.1257	0.3725	0.4140	6*
H44	−0.0019	0.4155	0.3781	6*
H45	0.4106	0.3488	0.1402	6*
H46	0.3901	0.3085	0.0846	6*
H48C	0.3930	0.5350	0.0262	4*
H48A	0.3515	0.3955	0.0295	4*
H48B	0.2680	0.5087	0.0273	4*
H49	0.3316	0.6856	0.0705	6*
H50	0.3594	0.7104	0.1273	6*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Asterisk identifies atom refined isotropically.

solved by MULTAN [16], which revealed the position of the cobalt atom. It was quickly found that the compound did not contain the expected tetradentate Cl_4Me_4salam, but rather the bidentate Cl_4Me_4salam with four coordinated picolines instead of two. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were found in difference Fourier syntheses. All hydrogens on C were adjusted to ideal calculated positions. However those on N and O were left as found, but not refined. A picoline and a water of solvation were also found, with the picoline disordered in the ratio 75%:25% over two slightly different locations. The isotropic thermal parameters of the disordered atoms were held fixed to facilitate refinement. After all shift/e.s.d. ratios were less than 0.2 (except for those involving the disorder), convergence was reached at the agreement factors listed in Table I. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than 0.30 e Å^{-3}. The hydrogens on N were both found to participate in intramolecular hydrogen bonds, which accounts for the observed gross configuration of the compound. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. The final positional parameters are listed in Table II.

Results and Discussion

Synthesis of the Cobalt(II) Complexes of Salam

SalamH_2 (*N,N'*-bis-salicyl-1,2-ethylenediamine) was prepared from acetylsalicylic acid and 1,2-ethylenediamine [11]. Likewise, we prepared the 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethyl analog from acetyl-3,5-dichlorosalicylic acid and 1,1,2,2-tetramethylethylenediamine [15]. The cobalt(II) complex **I** separated directly from solution as the light-purple sesquihydrate when Cl_4Me_4salamH_2 was mixed with cobaltous acetate in anhydrous methanol. It yielded the pale blue monohydrate upon drying *in vacuo* over phosphorus pentoxide, but slowly reverted to the purple solid on standing. In either form the complex was insoluble in water and all the common organic solvents including *N,N*-dimethylformamide and dimethylsulfoxide. The X-ray powder pattern of the sesquihydrate indicated it to consist largely of amorphous material (see 'Experimental'). Attempts to grow single crystals of **I** by the controlled addition of either component to the other in different combinations of solvents were unsuccessful. However $Co^{II}(Cl_4Me_4$salam) slowly dissolved in neat pyridine and 4-picoline when suspensions were stirred for prolonged periods. Attempts to isolate the pyridine adduct from the red–brown solution only led to an amorphous brown solid. Similarly when cobaltous acetate was added directly to Cl_4Me_4salamH_2 in methanol containing excess pyridine, the blue solution slowly took on a red coloration, but only the same amorphous brown adduct was obtained. Finally the 4-picoline adduct was isolated as an orange–red crystal (**II**) by the slow diffusion of hexane into the solution of Co(Cl_4Me_4salam)·3/2H_2O in 4-picoline.

X-ray Crystal Structure of $Co^{II}(Cl_4Me_4$salam)(picoline)$_4$

The cobalt(II) complex of Cl_4Me_4salam^{2-} crystallized from 4-picoline (pic) as the tetrakis adduct (**II**) and associated with an extra picoline and a water of solvation, *i.e.* $Co^{II}(Cl_4Me_4$salam)(pic)$_4$·pic·H_2O. In the crystal, the single picoline of solvation was disordered in two slightly different locations in a 75%:25% relative population. Otherwise the quality

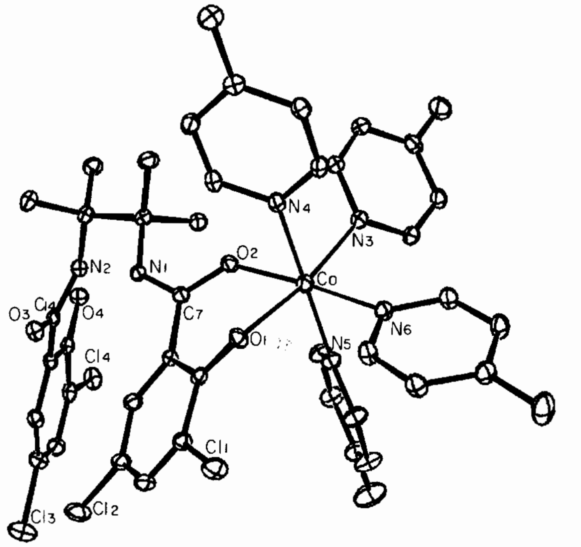
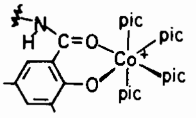


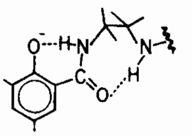
Fig. 1. ORTEP diagram of the picoline adduct II of Co^{II}-(Cl_4Me_4salam) showing the coordination of the diamide as a η^2-β-ketoenolate ligand. Hydrogens are omitted for clarity.

of the diffraction data was such as to allow all the nonhydrogen atoms to be refined and all the hydrogens to be located in the difference map. As shown in the ORTEP diagram (Fig. 1), the molecule consists of a cobalt bonded to four picolines and to only one-half of the salam ligand. Furthermore that part of salam which is utilized in complex formation involves just the phenolic and the carbonyl oxygens. Viewed in this way the cationic cobalt(II) moiety consists of an octahedral N_4O_2-coordination in which all four of the nitrogen ligands derive from 4-picoline – the pair of nitrogens in salam being innocent bystanders. The oxygen coordination arises from the salicyl fragment acting as a chelating β-ketoenolate ligand, *i.e.*



which is structurally equivalent to the more commonly known acac ligand. The utilization of the carbonyl oxygen rather than the amide nitrogen in chelation represents an important structural feature of the salicylamide function in **II** [17, 11, 12]. Indeed the driving force for the conversion of structure **I** to **II** can be attributed to the formation of an octahedral N_4O_2–cobalt cation as an intact stable structural unit [18]. If so, the remainder of the salam ligand must be stabilized as monoanion, so as to exist overall as a zwitter-ionic molecule.

Two hydrogen bonds play an important role in stabilizing the uncomplexed portion of the Cl_4Me_4-salam ligand, *i.e.*



the ORTEP diagram of which is emphasized by the perspective in Fig. 2. First, the intramolecular hydrogen bond binds the phenolic oxygen (O4) and the amide nitrogen (N2), which are separated by 2.6 Å with a H2–O4 distance of only 1.6 Å. Second, the carbonyl oxygen (O3) is hydrogen bonded to the amide nitrogen (N1), which are separated by 2.8 Å with a H1–O3 distance of 1.8 Å. The latter is largely responsible for the Cl_4Me_4salam ligand to be bent with the dihedral angle described by the two salicylamide planes to be ~45°. By comparison with NH. . . O bond distances found in other structures [20], both hydrogen bonds in **II** are short. Thus we believe that hydrogen bonding exerts an important stabilizing effect on the uncomplexed salicylamide extant in the cobalt(II) complex. See 'Supplementary Material'.

Comments on the Structure of Co^{II}(Cl_4Me_4salam) (I)

Owing to its insolubility and amorphous nature, it is not possible to ascertain with certainty how the salam is coordinated to cobalt(II) in complex **I**. In general, the coordination of an amide ligand to metal centers through either the oxygen or nitrogen atom is indicated by spectral shifts in the IR bands of the carbonyl group. For example, the coordination via the amide oxygen is indicated by the lowering of the carbonyl frequency by 30–80 cm^{-1}, whereas a smaller shift of <30 cm^{-1} is observed when coordination occurs via the amide nitrogen [21, 22]. Thus the shift in the carbonyl frequency from 1644 cm^{-1} in the free ligand $Cl_4Me_4salamH_2$ to 1620 cm^{-1} in the cobalt complex **I** is indicative of the core structure **A**

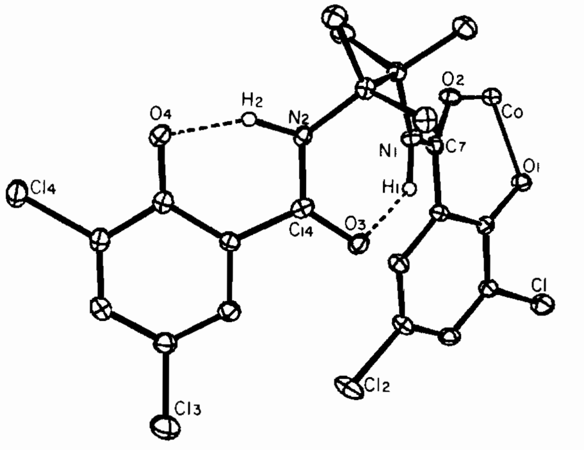


Fig. 2. ORTEP diagram of the hydrogen bonding extant in the pendant salicylamide moiety of **II**. The picoline coordination about the cobalt and the aromatic hydrogens are omitted for clarity.

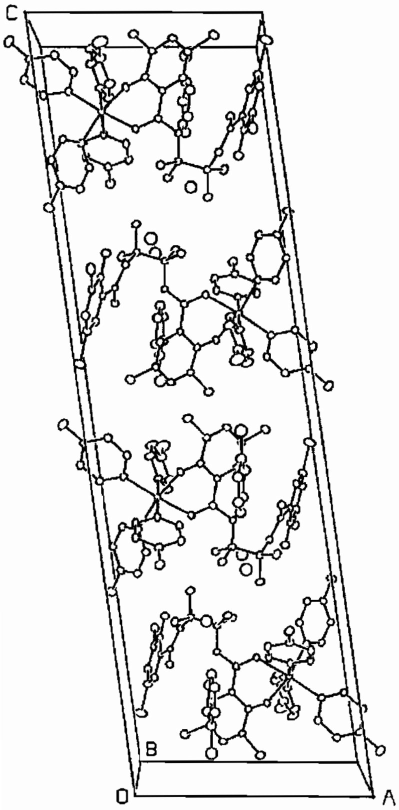


Fig. 3. Packing diagram in the unit cell of $Co^{II}(Cl_4Me_4salam)(pic)_4$. The uncomplexed picoline and water of solvation are omitted for clarity.

(*vide supra*). This conclusion is also in accord with the relative donor properties of the nitrogen and oxygen atoms in amide groups, since protonation and theoretical studies indicate that the amide nitrogen is more basic than the amide oxygen in acrylamides [22].

The base-induced conversion of **I** to the picoline adduct (**II**) represents a ligand rearrangement from tetradentate N_2O_2-coordination of cobalt to the bidentate structure shown in Fig. 1. Such a change in ligand coordination induced by pyridine bases has not been observed in the corresponding salen complexes [2, 7]. Thus square-planar salen metal complexes merely add one or two pyridines to the axial positions in order to complete the octahedral coordination [8]. The difference from salen may arise in part from the weaker donor properties of salam ligands as a result of converting an imino nitrogen to an amide nitrogen in line with their relative base strengths [19]. It is conceivable that the driving force for such a change is enhanced when it is coupled with the stabilization of the pendant salicylamido moiety, as emphasized in Fig. 2. We hasten to add however that this simplistic formulation does not properly take into account the extensive and varied intermolecular interactions which are undoubtedly extant in the parent complex **I** and contribute to its insolubility and amorphous character.

Supplementary Material

Tables of bond distances and angles are available on request.

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