only two metals.[10] The ligand employed here, $[H_2(DPE)](NH_2)_2$, consists of two β-alanyl appendages, positioned on one face of the porphyrin plane, which serve as chelating sites for additional metals. This is a flexible system designed to promote the formation of trimetallic complexes. Thus, when a central metal is chelated by a pair of these ligands, formation of linear trinuclear arrays is possible. Synthetically, it is convenient to insert a metal into the porphyrin core of $[H_2(DPE)](NH_2)_2$ in the first step. Subsequent introduction of an additional metal to link two porphyrin complexes affords the desired trinuclear complexes.

Preparation of $[\{[Ni(DPE)](NH_2)_2\}_2Zn](ClO_4)_2$ was achieved by following the above strategy. The solution ^1H NMR spectrum of this species clearly indicates that a new complex has formed. The presence of one resonance at 2.19 ppm (s) for the four pyrrole methyl substituents, one diastereotopic CH_2 multiplet at 3.62 ppm, and one triplet at 1.55 ppm for the four pyrrole ethyl groups indicates that the porphyrin ligand retains its C_2 symmetry in this complex. This is consistent with the expected tetrahedral geometry involving the central d^{10} zinc ion.

The trimetallic nature of all of the complexes described here has been confirmed by molecular weight measurements. Unfortunately, the trinuclear complexes reported here have not yet been amenable to mass spectral or X-ray diffraction analysis. However, a particularly useful alternative was the use of Cu(II) as the central, linking metal in this system and as an EPR probe for structure and composition. Thus $\{[Zn(DPE)](NH_2)_2\}_2CuCl_2$ exhibits an EPR spectrum with $a_{Cu} = 197.5$ G, $g_{\parallel} = 2.21$, and $g_{\perp} = 2.07$. This is consistent with an axially symmetric complex.[11] In addition, the nine-line ^{14}N superhyperfine splitting requires that four nitrogens bind to Cu in equivalent positions. These EPR data unambiguously indicate that the structure of the Cu core must be tetragonal, with chlorides occupying the axial positions and the four terminal amines of the two $[Ni(DPE)](NH_2)_2$ chelates residing in the equatorial plane.

Conclusions

Preparation of trinuclear species generally leads to the formation of triangular complexes.[12] Few rational methods for preparing linear trinuclear complexes are known, and these are not readily extendable to more than one type of metal system.[13] With the use of specially designed ligands, we have devised a general method for the synthesis of linear arrays of transition-metal complexes. The versatility of our multichelating ligands demonstrates that controlled syntheses of complex multinuclear molecules are readily achievable. For example, by judicious choice of metals, a series of homo- and heteronuclear trimetallic complexes can be prepared. Furthermore, additional modification can be achieved by altering the axial ligands bound to the central metal of these complexes. The compounds prepared here can be viewed as truncated portions of one-dimensional chains. Thus, in principle, it should be possible to prepare increasingly sophisticated materials with deliberately tailored properties. Further investigation of the physical and chemical properties of these novel complexes as well as extension of this work to polymeric systems is underway.

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Registry No. **1**, 136804-60-9; **2**, 136804-61-0; $\{[Ni(DPE)](NH_2)_2\}_2CuCl_2$, 136804-62-1; $\{[Cu(DPE)](NH_2)_2\}_2CuCl_2$, 136804-63-2; $\{[Ni(DPE)](NH_2)_2\}_2Cu(SCN)_2$, 136804-64-3; $[Ni(DPE)](NH_2)_2$, 136049-49-5; $[Zn(DPE)](NH_2)_2$, 136049-47-3; $[Cu(DPE)](NH_2)_2$, 136049-48-4.

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Nuclearity and Formulation of $SALPN^{2-}$ Complexes Formed from $M(O_2CCH_3)_2$: Resolution of Longstanding Problems by X-ray Crystallography

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Introduction

As part of a program aimed at understanding the synthesis and properties of organocobalt complexes relevant to B_{12} coenzymes, we have been investigating the synthesis of complexes based on quadridentate bis(salicylidene) Schiff base ligands.[1,2] Metal complexes of such quadridentate Schiff base ligands have been studied extensively, both as B_{12} models[1-3] and also because of the rich coordination chemistry generated by the well-known ability of the two coordinated phenolate oxygen atoms to bridge metal centers.[4] Further interest in these complexes has focused on their usefulness in studying magnetic exchange interactions between bridged paramagnetic metal ions[5,6] and on their application in catalytic processes.[7]

During the course of the investigation, we planned to prepare complexes based on $SALPN^{2-}$ (the dianion of *N,N'*-bis(salicylidene)propylenediamine) and $2,2\text{-}Me_2SALPN^{2-}$ (the dianion of *N,N'*-bis(salicylidene)-2,2-dimethylpropylenediamine). The preparation of $SALPN^{2-}$ complexes from $M(O_2CCH_3)_2$ has been reported to yield analytically impure products for Co(II)[8] and Fe(II)[9]. This type of preparation for Fe(II) has been reported to give a polymeric product on the basis of Mössbauer data,[10] but the reported analytical results cannot be considered acceptable.

In initial studies, we successfully prepared Co(II) complexes of the $SALPN^{2-}$ class of ligands from $Co(O_2CCH_3)_2$. Considering previous uncertainty concerning the nuclearity of the Fe(II) species,[10] we extended our synthetic methods to Fe(II) compounds.

Two complexes, formulated as $Co_3(SALPN)_2(O_2CCH_3)_2\cdot 2DMF$ (**1**) and $Fe_3(SALPN)_2(O_2CCH_3)_2\cdot 2DMF$ (**2**), were isolated as well-formed crystals. We undertook the structure determination of the complexes in order to establish the coordination geometry about the metal ions. Compounds **1** and **2** proved to have the same trimeric structure, with the metal ions in the +2 oxidation state. The only trimeric structures so far reported with

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Table I. Crystallographic Data for $Co_3(SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$ (**1**) and $Fe_3(SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$ (**2**)

	1	**2**
chem formula	$C_{44}H_{52}N_6O_{10}Co_3$	$C_{44}H_{52}N_6O_{10}Fe_3$
fw	1001.7	992.5
space group	*Fdd*2	*Fdd*2
a, Å	11.478 (2)	11.558 (3)
b, Å	26.993 (5)	26.89 (1)
c, Å	30.07 (6)	30.13 (1)
V, $Å^3$	9316 (3)	9365 (5)
Z	8	8
T, °C	24	24
λ(Mo Kα), Å	0.71073	0.71073
abs coeff, mm^{-1}	1.113	0.975
ρ_{calc}, g cm^{-3}	1.428	1.408
final *R* (R_w)	0.031 (0.043)	0.037 (0.048)

a $SALPN^{2-}$-type ligand are for a mixed-oxidation-state cobalt trinuclear complex, $[Co^{II}Co^{III}_2(SO_3)_2(L)_2(Pr^nOH)_2] \cdot Pr^nOH$ (where L is a $SALPN^{2-}$ derivative in which the two imine protons in $SALPN^{2-}$ are replaced by two methyl groups),[11] and for two heteronuclear complexes, $[ZnCu_2(SALPN)_2(O_2CCH_3)_2]$[12] and $[C_2H_9O_2][NaMn_2(2\text{-}OH\text{-}SALPN)_2(O_2CCH_3)_4] \cdot 2H_2O$[6] (where 2-OH-$SALPN^{2-}$ is the dianion of the Schiff base ligand *N*,*N*′-bis(salicylidene)-2-hydroxypropylenediamine).

Experimental Section

Magnetic moments were measured with a Johnson Matthey magnetic susceptibility balance. SALPN and 2,2-Me_2SALPN were prepared by condensation of 1,3-diaminopropane and 2,2-dimethyl-1,3-diaminopropane, respectively, with salicylaldehyde in methanol.[13] $Fe(O_2CCH_3)_2 \cdot 4H_2O$ was synthesized under dinitrogen from the metal and acetic acid.[14] $Co(O_2CCH_3)_2 \cdot 4H_2O$ was obtained from Baker. The following preparations were carried out under a pure dinitrogen atmosphere. Dry DMF was degassed prior to use.

$M_3(SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$ (M = Co(II) (1), Fe(II) (2)). Pure DMF solvent (7 mL) was layered on a solution of $M(O_2CCH_3) \cdot 4H_2O$ (0.17 g, 0.708 mmol) in DMF (7 mL). Then a solution of SALPN (0.2 g, 0.708 mmol) in DMF (7 mL) was added as a top layer. After 24 h, X-ray-quality crystals were collected. Total yields: 0.2 g (85%) for M = Co(II); 0.15 g (65%) for M = Fe(II). Anal. Calcd for $C_{38}H_{38}N_4O_8Co_3 \cdot 2DMF$: C, 52.78; H, 5.23; N, 8.39. Found: C, 52.70; H, 5.25; N, 8.35. Calcd for $C_{38}H_{38}N_4O_8Fe_3 \cdot {}^7/_8DMF$: C, 53.58; H, 4.88; N, 7.50. Found: C, 53.59; H, 4.65; N, 7.13.

$Fe_3(2,2\text{-}Me_2SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$ (3). This compound was prepared as above using 2,2-Me_2SALPN (0.2 g, 0.644 mmol). The dark red microcrystals that formed after 1 day were collected, rinsed with diethyl ether, and vacuum-dried. Yield: 0.12 g (48%). Anal. Calcd for $C_{42}H_{46}N_4O_8Fe_3 \cdot 2DMF$: C, 54.88; H, 5.95; N, 8.00. Found: C, 54.63; H, 5.79; N, 7.75.

Collection and Reduction of X-ray Data. Single efflorescent crystals of **1** and **2** obtained as described above were mounted in glass capillaries under a dinitrogen atmosphere together with some DMF in order to prevent disintegration of the crystals. Data collection was carried out at ambient temperature on a Nicolet P3F automated four-circle diffractometer equipped with a graphite monochromator. Unit cell parameters were determined on the basis of 25 accurately centered reflections (15° ≤ 2θ ≤ 30°). The crystal data of interest are given in Table I. Intensities of 2 check reflections measured after every 124 reflections during the data collection did not show any systematic decay throughout data monitoring. The data were corrected for absorption, by the semiempirical method using ψ scans, as well as for Lorentz and polarization effects.

Structure Solution and Refinement. Both structures **1** and **2** were solved by conventional heavy-atom techniques. The metal atoms were located by Patterson syntheses using the program SHELXS-86.[15] Full-matrix least-squares refinement and difference Fourier methods using SHELX-76[16] and Siemens SHELXTL PLUS (VMS) were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from a standard source.[17] In both **1** and **2** the unique DMF molecule was found to be disordered. The disorder was interpreted as due to two molecular orientations of occupancy 0.5. All non-hydrogen atoms except

Table II. Atom Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for $Co_3(SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$

atom	*x*	*y*	*z*	$U_{equiv}{}^a$
Co(1)	0	0	0	39 (1)
Co(2)	−1677 (1)	887 (1)	−34 (1)	39 (1)
O(1)	−1123 (4)	353 (1)	−457 (1)	47 (1)
O(2)	−1103 (3)	393 (1)	438 (2)	46 (1)
O(3)	1082 (3)	624 (1)	−5 (2)	53 (1)
O(4)	−111 (3)	1273 (1)	−46 (2)	52 (1)
O(5)	−3436 (3)	531 (1)	−56 (2)	71 (1)
N(1)	−2297 (4)	1301 (2)	−562 (2)	45 (1)
N(2)	−2408 (4)	1310 (2)	462 (2)	44 (1)
C(1)	−2352 (5)	1132 (2)	−964 (2)	52 (2)
C(2)	−2663 (6)	1810 (2)	−482 (2)	58 (2)
C(3)	−3428 (5)	1852 (2)	−76 (3)	53 (2)
C(4)	−2780 (6)	1819 (2)	368 (2)	56 (2)
C(5)	−2693 (5)	1119 (2)	843 (2)	49 (2)
C(6)	870 (4)	1070 (2)	−36 (2)	51 (2)
C(7)	1911 (6)	1424 (2)	−84 (5)	99 (4)
C(12)	−2432 (5)	638 (2)	1010 (2)	44 (2)
C(22)	−1689 (4)	288 (2)	805 (2)	43 (2)
C(32)	−1574 (5)	−180 (2)	1010 (2)	53 (2)
C(42)	−2167 (6)	−298 (2)	1390 (2)	60 (2)
C(52)	−2897 (6)	41 (3)	1596 (2)	62 (2)
C(62)	−3003 (6)	508 (2)	1407 (2)	57 (2)
C(11)	−2035 (5)	650 (2)	−1124 (2)	50 (2)
C(21)	−1482 (5)	271 (2)	−868 (2)	47 (2)
C(31)	−1324 (6)	−195 (2)	−1064 (2)	58 (2)
C(41)	−1619 (6)	−274 (3)	−1507 (3)	69 (2)
C(51)	−2100 (7)	85 (3)	−1757 (2)	73 (3)
C(61)	−2309 (6)	550 (3)	−1573 (2)	65 (2)
C(8A)	−3526 (10)	72 (4)	155 (4)	52 (3)
C(8B)	−3492 (9)	116 (4)	−275 (4)	44 (2)
C(9A)	−4388 (14)	−609 (6)	575 (6)	78 (4)
C(9B)	−5161 (16)	379 (6)	−775 (6)	79 (4)
C(10A)	−5197 (15)	254 (6)	623 (6)	80 (4)
C(10B)	−4358 (20)	−551 (9)	−689 (8)	106 (7)
N(3A)	−4349 (9)	−76 (4)	441 (4)	54 (2)
N(3B)	−4319 (10)	−13 (4)	−565 (4)	63 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

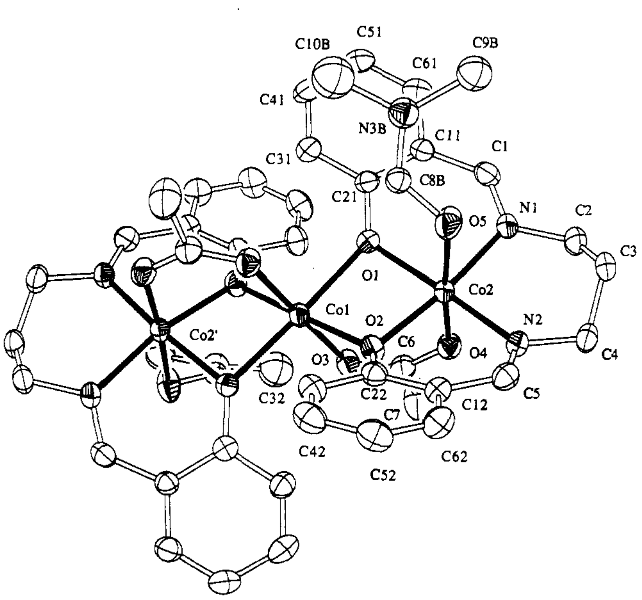

Figure 1. ORTEP drawing (30% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of **1**.

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Table III. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $Fe_3(SALPN)_2(O_2CCH_3)_2 \cdot 2DMF$

atom	*x*	*y*	*z*	U_{equiv}[a]
Fe(1)	0	0	0	41 (1)
Fe(2)	−1664 (1)	886 (1)	−33 (1)	42 (1)
O(1)	−1161 (5)	356 (2)	−462 (2)	51 (2)
O(2)	−1149 (4)	393 (2)	458 (2)	47 (2)
O(3)	1084 (4)	623 (2)	4 (2)	57 (2)
O(4)	−82 (4)	1281 (2)	−42 (2)	54 (1)
O(5)	−3474 (4)	521 (2)	−47 (3)	75 (2)
N(1)	−2272 (6)	1294 (2)	−567 (2)	47 (2)
N(2)	−2408 (5)	1315 (2)	476 (2)	44 (2)
C(1)	−2371 (7)	1127 (3)	−968 (3)	51 (3)
C(2)	−2664 (8)	1814 (3)	−481 (3)	59 (3)
C(3)	−3422 (7)	1848 (2)	−77 (3)	56 (2)
C(4)	−2795 (8)	1823 (3)	368 (3)	58 (3)
C(5)	−2716 (6)	1131 (3)	855 (3)	50 (2)
C(6)	883 (6)	1081 (2)	−29 (3)	54 (2)
C(7)	1926 (7)	1415 (3)	−77 (6)	105 (5)
C(12)	−2457 (7)	639 (3)	1027 (2)	47 (2)
C(22)	−1713 (6)	295 (3)	826 (3)	42 (2)
C(32)	−1597 (7)	−182 (3)	1032 (3)	56 (3)
C(42)	−2186 (7)	−301 (3)	1410 (3)	61 (3)
C(52)	−2902 (8)	49 (3)	1617 (3)	63 (3)
C(62)	−3028 (7)	512 (3)	1422 (3)	60 (3)
C(11)	−2050 (7)	642 (3)	−1130 (3)	53 (2)
C(21)	−1505 (7)	266 (3)	−872 (3)	49 (3)
C(31)	−1335 (8)	−203 (3)	−1068 (3)	58 (3)
C(41)	−1613 (7)	−279 (3)	−1509 (3)	68 (3)
C(51)	−2096 (9)	85 (4)	−1762 (3)	76 (4)
C(61)	−2324 (8)	540 (3)	−1577 (3)	65 (3)
C(8A)	−3545 (15)	64 (6)	175 (6)	60 (4)
C(8B)	−3524 (15)	120 (6)	−264 (6)	57 (4)
C(9A)	−5197 (19)	255 (8)	646 (7)	80 (6)
C(9B)	−4368 (26)	−529 (11)	−687 (10)	107 (9)
C(10A)	−4409 (19)	−601 (8)	604 (8)	84 (6)
C(10B)	−5150 (20)	388 (8)	−773 (7)	80 (6)
N(3A)	−4362 (14)	−104 (5)	463 (5)	64 (4)
N(3B)	−4352 (13)	−12 (6)	−561 (5)	68 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) in $Co_3(SALPN)_2(O_2CCH_3)_2(DMF)_2$ (**1**) and $Fe_3(SALPN)_2(O_2CCH_3)_2(DMF)_2$ (**2**)

Co(1)–O(1)	2.110 (4)	Fe(1)–O(1)	2.157 (5)
Co(1)–O(2)	2.113 (4)	Fe(1)–O(2)	2.187 (5)
Co(2)–N(1)	2.070 (5)	Fe(2)–N(1)	2.070 (6)
Co(2)–N(2)	2.057 (5)	Fe(2)–N(2)	2.104 (6)
Co(2)–O(1)	2.025 (4)	Fe(2)–O(1)	2.010 (5)
Co(2)–O(2)	2.055 (4)	Fe(2)–O(2)	2.074 (5)
Co(1)–O(3)	2.094 (3)	Fe(1)–O(3)	2.093 (5)
Co(2)–O(4)	2.077 (3)	Fe(2)–O(4)	2.116 (5)
Co(2)–O(5)	2.236 (4)	Fe(2)–O(5)	2.311 (5)
O(1)–Co(1)–O(2)	79.2 (2)	O(1)–Fe(1)–O(2)	79.3 (2)
O(1)–Co(2)–O(2)	82.6 (2)	O(1)–Fe(2)–O(2)	85.5 (2)
O(1)–Co(2)–N(1)	90.6 (2)	O(1)–Fe(2)–N(1)	88.6 (2)
O(2)–Co(2)–N(2)	88.0 (2)	O(2)–Fe(2)–N(2)	87.0 (2)
N(1)–Co(2)–N(2)	89.5 (2)	N(1)–Fe(2)–N(2)	97.9 (2)
Co(1)–O(1)–Co(2)	96.0 (2)	Fe(1)–O(1)–Fe(2)	94.6 (2)
Co(1)–O(2)–Co(2)	95.0 (2)	Fe(1)–O(2)–Fe(2)	91.9 (2)

the three carbons and one nitrogen on the DMF molecule were refined with anisotropic thermal parameters. Hydrogen atoms were included on well-ordered carbons at calculated positions by using a riding model with C–H = 0.96 Å and $U_H = 1.2U_C$. Final *R* and R_w values are given in Table I. The function minimized was $\sum w(F_o - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0.001F_o^2]$. Final positional parameters are given in Tables II and III. Complete listings of thermal parameters, bond distances, and bond angles are included as supplementary material.

Results and Discussion

An ORTEP[18] drawing of molecule **1**, including the atom-labeling scheme, is shown in Figure 1.

Complexes **1** and **2** are structurally equivalent. Co(2) and Co(2′) are related by a 2-fold axis passing through Co(1) and in the plane of the four phenoxide oxygen atoms. The pseudooctahedral coordination geometry of the central metal ion consists of four bridging oxygen atoms from two $SALPN^{2-}$ ligands and an oxygen atom from each of the two bridging O_2CCH_3 ligands occupying the axial positions.

The terminal metal ions have pseudooctahedral coordination. The $SALPN^{2-}$ ligand occupies the four equatorial positions, and the two apical positions are occupied by the oxygen atom of the bridging acetate and by a DMF molecule.

The $SALPN^{2-}$ ligand has an umbrella-shaped conformation. The dihedral angle between the salicylaldimine residue N(1), C(1), C(11)···C(61), O(1) and the plane N(1), N(2), O(1), O(2) is 19.3° for compound **1** and 19.1° for compound **2**. The dihedral angle between the other salicylaldimine residue, N(2), C(5), C(12)···C(62), O(2), and the plane N(1), N(2), O(1), O(2) is 31.7° for compound **1** and 31.3° for compound **2**. The four $SALPN^{2-}$ donor atoms are coplanar within ±0.042 (3) Å for both **1** and **2**. The metal atom is displaced out of this plane toward O(4) by 0.119 Å (**1**) and 0.145 Å (**2**). Selected bond distances and angles for compounds **1** and **2** are given in Table IV.

The Fe(2)–N($SALPN^{2-}$) bond distances fall within the range known for mononuclear Fe–$SALEN^{2-}$ complexes (2.085–2.101 Å)[14,19] (SALEN = *N,N′*-bis(salicylidene)ethylenediamine), but the Fe(2)–O($SALPN^{2-}$) distances are significantly longer (ranging from 1.951 to 1.960 Å), reflecting the bridging nature of this phenoxide oxygen atom relative to terminal coordination in mononuclear complexes.[3]

The Co–N and Co–O bond lengths between Co(2) and $SALPN^{2-}$ are approximately 0.2 Å longer than those observed in Co(SALEN)·$CHCl_3$ (Co–N = 1.847 Å, Co–O = 1.852 Å).[20] This difference can be explained by the octahedral coordination around the metal ion in **1** compared to the square-planar arrangement in the $SALEN^{2-}$ derivative. These distances are also significantly longer than those between Co(III) and the nitrogen and oxygen atoms of a $SALPN^{2-}$ derivative in $[Co^{II}Co^{III}_2(SO_3)_2(L)_2(Pr^nOH)_2] \cdot Pr^nOH$.[11] This variation is expected because of the larger Shannon radius of Co(II) (0.885 Å) compared to Co(III) (0.75 Å).[21]

The geometrical arrangement of **1** and **2** is similar to that of the mixed-metal trinuclear complex $[C_2H_9O_2][NaMn_2(2\text{-}OH\text{-}SALPN)_2(O_2CCH_3)_4] \cdot 2H_2O$.[6] In this species, monodentate acetate ligands replace the monodentate DMF molecules in **1** and **2**.

The magnetic moments μ_M for non-spin-coupled Co(II)($S = {}^3/_2$)–Co(II)($S = {}^3/_2$)–Co(II)($S = {}^3/_2$) and Fe(II)($S = 2$)–Fe(II)($S = 2$)–Fe(II)($S = 2$) systems can be derived from the equation $\mu_M{}^2 = \sum \mu_i{}^2$, where μ_i are the magnetic moment values for monomeric high-spin Co(II) (octahedral) (4.3–5.2 μ_B) and Fe(II) (octahedral) (5.1–5.7 μ_B) complexes.[12,22] Estimated values for a non-spin-coupled three-M system are in the ranges 7.5–9.0 μ_B for Co(II), and 8.8–9.9 μ_B for Fe(II). The observed magnetic moments of 8.2 μ_B (**1**), 9.6 μ_B (**2**), and 9.6 μ_B (**3**) at room temperature fall in the respective estimated ranges. Accordingly, it is presumed that the magnetic interaction between any pair of metal atoms is either negligible or nonexistent. However, a variable-temperature study of the magnetic behavior of both **1** and **2** is clearly needed to verify these conclusions.

Separation of the two Mn(III) ions in $[C_2H_9O_2][NaMn_2(2\text{-}OH\text{-}SALPN)_2(O_2CCH_3)_4] \cdot 2H_2O$ by a sodium ion leads to no spin exchange between these two terminal ions.[6] Since both **1** and **2** are structurally similar to this trinuclear complex and (as our limited data suggest) possess similar magnetic properties, a more

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detailed investigation of magnetic behavior would be of interest; the correlation between bridging structure and spin coupling for this class of trimeric compounds would become evident in such a study.

Finally, the recognized difficulty in the isolation of analytically pure samples of monomeric MSALPN complexes with M-$(O_2CCH_3)_2$[8,9] may be attributed to the presence of some acetate-bridged species. We find that acetate is present in the preparations carried out with other metal ions and other related Schiff base ligands. Analytically pure monomeric FeSALPN has been prepared from $Fe(CO)_5$.[9] The Mössbauer parameters of this well-characterized species differ significantly from "FeSALPN" prepared from $Fe(O_2CCH_3)_2$,[10] possibly because of the presence of species such as **2**.

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Registry No. **1**, 136804-08-5; **2**, 136804-09-6; **3**, 136804-10-9.

Supplementary Material Available: An ORTEP drawing of molecule **2** and crystal packing diagrams and tables giving details of the X-ray structural analysis, bond lengths and bond angles, calculated hydrogen atom coordinates, and anisotropic thermal parameters for complexes **1** and **2** (12 pages); listings of observed and calculated structure factors for complexes **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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A Zinc Complex of the Carbonic Anhydrase Inhibitor Acetazolamide (aaaH): Crystal Structure of $(aaa)_2Zn(NH_3)_2$

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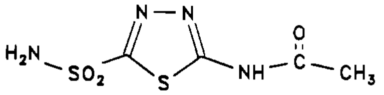
Introduction

The widely varying and well-known role of zinc in many biological processes contrasts sharply with the small number of simple zinc complexes which can serve as functional or structural models thereof. We have therefore set out to provide structural information in order to facilitate a relevant discussion at the molecular level. An attractive compound for such studies is the enzyme carbonic anhydrase (CA), whose structure and function are simple: its ligation of the zinc ion by three histidine imidazoles can be modeled by tridentate ligands,[1] and models of its CO_2 hydrating function begin to emerge.[2]



1 = aaaH

Among the many inhibitors, mostly anionic ones, of CA, acetazolamide (aaaH, **1**) is the most prominent one. The structure of the enzyme–inhibitor complex has been determined at 3 Å resolution, and that of the enzyme–(3-(acetoxymercurio)-4-aminobenzenesulfonamide) complex at 2 Å resolution.[3] In both cases, the inhibitors act as monodentate ligands through their amidosulfonyl moieties. While the protein crystallographic data cannot differentiate between Zn–N and Zn–O binding, it has been shown by a variety of methods that the inhibitors bind to zinc through their sulfonamide N atoms.[4] Up to now, these findings have not been complemented by the structure of a simple metal complex of acetazolamide: in the nickel complex one of the ring nitrogens and in the copper complex the amide nitrogen as well as both ring nitrogens ligate the metal.[5] The simplest model compound, $(aaa)_2Zn(NH_3)_2$ (**2**), first obtained by Borrâs,[6] was reported to be difficult to crystallize. We have now obtained crystalline **2**. This paper reports its structure.

Table I. Crystallographic Data for **2**

chem formula	$C_8H_{16}N_{10}O_6S_4Zn$
mol wt	542.0
space group	*Pbcn* (No. 60)
cell	a = 7.055 (1) Å, b = 10.083 (1) Å, c = 27.703 (3) Å
V	1970.8 (3) Å^3
Z	4
ρ_{obsd}, ρ_{calcd}	1.70, 1.68 g cm^{-3}
μ(Mo Kα)	16.30 cm^{-1}
T	20 °C
λ(Mo Kα)	0.71073 Å
R(unit weights)	0.051

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors for **2**

atom	x	y	z	U_{eq}, Å^2
Zn	0.0000	0.5802 (1)	0.2500	0.033 (1)
N1	−0.1504 (8)	0.4638 (6)	0.2046 (2)	0.047 (2)
N2	0.1804 (8)	0.6849 (5)	0.2109 (2)	0.037 (2)
S1	0.3395 (2)	0.6177 (2)	0.1814 (1)	0.033 (1)
O1	0.5093 (7)	0.6957 (5)	0.1751 (2)	0.046 (2)
O2	0.3659 (7)	0.4844 (4)	0.1997 (2)	0.046 (2)
C1	0.2652 (10)	0.5979 (6)	0.1210 (2)	0.035 (2)
S2	0.3984 (3)	0.6528 (2)	0.0729 (1)	0.039 (1)
N3	0.1133 (9)	0.5321 (6)	0.1087 (2)	0.045 (2)
N4	0.0930 (9)	0.5234 (6)	0.0599 (2)	0.048 (2)
C2	0.2312 (10)	0.5819 (7)	0.0358 (2)	0.038 (2)
N5	0.2351 (9)	0.5847 (6)	−0.0121 (2)	0.042 (2)
C3	0.3736 (12)	0.6439 (8)	−0.0377 (3)	0.051 (3)
O3	0.5145 (9)	0.6851 (7)	−0.0169 (2)	0.073 (2)
C4	0.3460 (12)	0.6536 (9)	−0.0916 (3)	0.061 (3)

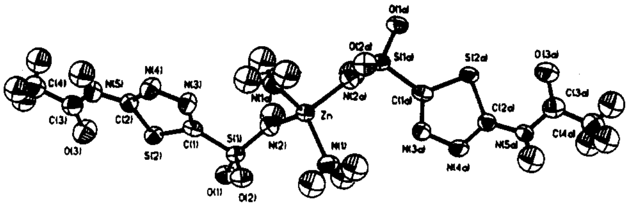


Figure 1. Thermal ellipsoid plot of the structure of **2**.

Experimental Section

Preparation. Colorless crystals of **2**[6] were obtained by dissolving **1** (500 mg, 2.24 mmol) and $Zn(ClO_4)_2$ (300 mg, 1.12 mmol) in 25% ammonia (5 and 6 mL, respectively). Both solutions were combined dropwise. Crystals were formed by slow room-temperature evaporation through a very small opening. After a period of 2 months, the yield was 516 mg (87%) of **2**.

Crystallographic Data Collection and Refinement of the Structure. Crystallographic data are summarized in Table I. The crystal used was colorless with a prismatic shape. The X-ray data were recorded with a CAD-4 Enraf-Nonius diffractometer using graphite-monochromated Mo Kα radiation. Cell dimensions were obtained by a least-squares fit from

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