a spin $^1/_2$ system with three unique g values, $g_1 = 2.2055$, $g_2 = 2.081$, and $g_3 = 2.062$. A computer-simulated spectrum[7] calculated using these parameters is also presented in Figure 3.

The electronic structure of $NiMNT^{3-}$ is a matter of considerable interest. Most workers are now agreed that the *dianion* approximates a Ni(II) in which the ligands each carry a charge of 2−. In an extension of this treatment,[2] the trianion would be expected to have an unpaired electron in an orbital of B_{1g} symmetry, composed of a metal in-plane d_{xy} orbital and sulfur in-plane p orbitals. This is the configuration favored in the esr studies of Maki, *et al.*,[8] for the formally isoelectronic $CuMNT^{2-}$, in which a high degree of metal-ligand delocalization is found. It is interesting to note, however, that the observed g-value anisotropy for $NiMNT^{3-}$ is much greater than that of the copper complex,[9] even though the spin-orbit coupling parameter is smaller for nickel. In fact, the spin-Hamilton parameters obtained from our esr spectra are reminiscent of those observed in genuine d^9 complexes[10] and argue strongly that the orbital containing the unpaired electron is largely metal in character. The observed g-value anisotropy cannot be accounted for if a large amount of spin density is located on the ligands.[11] Thus our data favor a d^9, or Ni(I), formulation for the metal in the bis(maleonitriledithiolato)nickel trianion. This is clearly consistent with the previous description of the corresponding dianion as containing Ni(II), provided that in the formation of the trianion a primarily metal-based orbital is involved.

Registry No. Bis(maleonitriledithiolato)nickel trianion, 38117-63-4; bis(maleonitriledithiolato)nickel dianion, 38123-73-8.

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Pentadentate Ligands. VI. Cobalt(II) Complexes of *N,N'*-Bis(salicylidene)-2,2'-bis(aminoethyl) Sulfide

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It is well known that cobalt(II) shows a more pronounced tendency for the formation of tetrahedral complexes than does either nickel(II) or copper(II).[2] This has been illustrated with bis-bidentate complexes[3] and metal complexes containing tetradentate ligands derived from salicylaldehyde[4,5] and pyrrole-2-carboxaldehyde[6] with various polymethylene diamines. For example the well-known oxygen-active complex *N,N'*-bis(salicylidene)ethylenediaminocobalt(II) exhibits an essentially low-spin square-planar structure.[7,8] An oxygen-inactive form has been shown to have square-pyramidal coordination about cobalt which is achieved by bridging an oxygen atom from a second Co(SALEN) molecule.[9] The analogous trimethylene derivative contains high-spin four-coordinate cobalt(II) in which a strongly distorted tetrahedral geometry has been suggested.[10] The corresponding cobalt(II) complexes with four to ten carbon atoms in the central chelate ring exhibit a regular tetrahedral geometry.[4,11]

Incorporation of a donor atom into the polymethylene bridge thereby forming a linear pentadentate ligand may produce interesting results concerning structure and reactivity at the metal site. Such factors as the ligand strength of the inserted donor, the length of the carbon bridge, and the metal ion involved should prove important. This report deals with the interaction of cobalt(II) with the linear potentially pentadentate ligands derived from substituted salicylaldehydes and 2,2'-bis(aminoethyl) sulfide, hereafter referred to as SALDAES, and the physical and chemical properties of the resulting complexes.

Experimental Section

Materials. 5-Bromosalicylaldehyde (5-BrSAL) was prepared by a method described previously.[12] 5-Methylsalicylaldehyde ($5\text{-}CH_3SAL$) was prepared by a modification of the Reimer-Tieman reaction.[12] 3-Isopropylsalicylaldehyde ($3\text{-}(CH_3)_2CHSAL$) was prepared according to the general procedure of the Duff[13] reaction starting with *o*-isopropylphenol. All other chemicals were of reagent grade or equivalent.

Preparation of the Cobalt(II) Complexes. The cobalt(II) complexes were prepared by several independent methods under nitrogen in order to ensure each sample's integrity. The general method of preparation was as follows. To a refluxing anhydrous ethanol or methanol solution (50 ml) of 0.01 mol of pentadentate Schiff base ligand[12] to which had previously been added 0.01 mol of triethyl orthoformate and 0.2 mol of triethylamine was added 0.01 mol of either $Co(C_2H_3O_2)_2 \cdot 4H_2O$ or $CoCl_2 \cdot 6H_2O$ dissolved in anhydrous methanol or ethanol (100 ml) which contained 0.025 mol of triethyl orthoformate. The reaction mixture was refluxed 1.5 hr and then allowed to come to room temperature. Red-brown to orange crystals appeared upon cooling, which were filtered under nitrogen, washed with a minimum amount of anhydrous ethanol, and dried *in vacuo* for 12 hr. The complexes could also be prepared by a coordinated ligand reaction by allowing a refluxing ethanol suspension of the appropriate bis(salicylaldehydo)cobalt(II) to react with DAES for 1 hr. Isolation and drying were as described above. The resulting complexes were normally analytically pure. Recrystallization, if desired, could be accomplished from hot *N,N*-dimethylformamide (DMF). Analytical data are presented in Table I.

Results and Discussion

Complexes of general formula $[Co(XSALDAES)] \cdot nH_2O$

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Table I. Analytical Data for the Cobalt(II) Complexes

Compound	% calcd			% found			Method of prepn[a]
	C	H	N	C	H	N	
Co(HSALDAES)·H_2O	53.60	4.96	6.94	53.84	4.99	6.74	B
				53.30	4.80	7.13	D
Co(5-BrSALDAES)	39.80	2.98	5.16	40.00	3.05	4.88	C
				39.86	3.05	5.06	A
Co(5-CH_3SALDAES)	58.10	5.37	6.78	57.89	5.46	6.76	C
				57.68	5.38	6.52	B
Co(5-CH_3SALDAES)·H_2O	55.63	5.57	6.50	55.87	5.70	6.78	A
Co(3-$(CH_3)_2$CHSALDAES)	61.38	6.45	5.96	61.39	6.22	6.00	B
				60.86	6.22	6.04	C
Co(5-NO_2SALDAES)·H_2O	43.81	3.65	11.38	43.61	3.57	11.25	C

[a] A = $CoCl_2$, ethanol; B = $Co(C_2H_3O_2)_2$, methanol; C = $Co(C_2H_3O_2)_2$, ethanol; D = $Co(Sal)_2 \cdot 2H_2O$ + DAES, ethanol.

Table II. Room-Temperature Magnetic Moments of the Cobalt(II) Complexes in the Solid State

Compound	μ_{eff},[a] BM
Co(HSALDAES)·H_2O	4.38–4.40
	4.28–4.29
Co(5-BrSALDAES)	4.52–4.58
	4.36–4.37
Co(5-CH_3SALDAES)	4.38–4.42
	4.60–4.68
Co(5-CH_3SALDAES)·H_2O	4.19–4.20
Co(3-$(CH_3)_2$CHSALDAES)	4.32–4.33
	4.41–4.47
Co(5-NO_2SALDAES)·H_2O	4.19–4.21

[a] Maximum and minimum values reported for μ_{eff} with field strengths ranging from 4000 to 11,000 G.

Table III. Near-Infrared–Visible Spectra of the Cobalt(II) Complexes (cm^{-1})[a]

Compound	Medium	Absorption maxima[b,c]		
		ν_2	ν_3	ν_4
Co(SALDAES)·H_2O	Nujol	10,200 vb	18,180	26,460
	$CHCl_3$	7900 (56), 11,660 (26)	17,630 sh (56)	27,390 (7100)
Co(5-CH_3SALDAES)	Nujol	8300, 10,580	18,100 sh, 19,610 sh	24,690
	$CHCl_3$	7950 (47), 11,720 (28)	17,700 sh (50)	26,670 (6500)
Co(3-$(CH_3)_2$CHSALDAES)	Nujol	8000, 11,590	17,540 sh, 20,000 sh	26,310
	$CHCl_3$	8260 (46), 12,050 (72)	17,860 (54)	26,810 (8190)
Co(5-NO_2SALDAES)	Nujol	9950 vb	18,100	25,320
	DMF	9950 vb (15)	*d*	25,330 (10,200)
Co(5-BrSALDAES)	Nujol	8300, 10,580	18,100 sh, 19,610 sh	24,690
	$CHCl_3$	*e*	*e*	26,670 (6980)

[a] Key: vb, very broad; sh, shoulder. [b] ν_1 not observed in the infrared region. [c] Numbers in parentheses are molar extinction coefficients. [d] Not observed. [e] Too insoluble to detect.

where n = 0 or 1 are isolated in each case. Only in the case of the 5-methyl derivative could both anhydrous and hydrated complexes be prepared. Heating the hydrated form at 120° *in vacuo* yielded the anhydrous material. The materials range in color from light brown to red. In the solid state and in solution, all the complexes appear to be quite air stable. Recrystallization from hot DMF in the air leaves the compounds unchanged as evidenced by magnetic measurements and elemental analysis.

The conclusions drawn from the infrared spectra of these materials taken in the form of Nujol mulls support the proposed formulation. A band with an accompanying shoulder is observed in the 1640–1620-cm^{-1} region which is indicative of a symmetric and asymmetric C=N stretching mode for a coordinated Schiff base linkage. The spectra of those compounds which are postulated to be hydrates exhibit a weak very broad band around 3400 cm^{-1} which strongly suggests the presence of noncoordinated water.

Poor solubility in an appropriate solvent made molecular weight measurements in solution impossible. However, being neutral materials the complexes possessed sufficient vapor pressure to give rise to interpretable mass spectra. The spectrum of each complex exhibits a relatively intense parent ion cluster. No peaks of any consequence appear above the parent ion cluster. The spectra were run at as low a temperature as possible in order to minimize any decomposition. The spectra of those compounds which are hydrates exhibited no cluster that corresponded to the parent plus water. At the temperature and pressure of the mass spectrometer dehydration probably precedes electron bombardment. These observations support a monomeric formulation for these complexes in the gas phase. The relatively good solubility of these materials in several solvents suggests a monomer in the solid state. These materials appear to fragment *via* two routes in a manner somewhat similar to Co(SALEN).[14,15] These processes are (1) simultaneous cleavage at one of the Co—O, Co—N, and C=N bonds with subsequent successive cleavage of the five-atom sulfur-containing chain and (2) stripping out of the five-atom chain in one or two fragmentation steps thereby maintaining the in-plane groups of atoms. Relatively intense doubly charged parent ion clusters also are found in the spectra which are indicative of the strong interaction that exist between metal and pentadentate ligand.

Room-temperature magnetic susceptibilities *via* the Faraday method have been measured on the complexes in the solid state. Table II lists the calculated effective magnetic moments for Co(XSALDAES). The measurements were taken in duplicate on each sample at four different field strengths. The agreement between preparations is reasonably good. The measured susceptibilities are essentially independent of the magnetic field strength. The moments fall in the range 4.2–4.7 BM which is typical of tetrahedral[16] or five-coordi-

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nate[17] cobalt(II) complexes. Octahedral complexes are ruled out on the grounds that a large orbital contribution is expected in the ground state which should cause μ_{eff} to fall in the range 4.8–5.6 BM.[16]

Near-infrared–visible spectra in the form of Nujol mulls have been measured and the observed absorption maxima are shown in Table III. Three and sometimes four bands are observed for each complex depending upon whether the broad band around 10,000 cm^{-1} is split into two components. The similarity between the visible spectra of Co(XSALDAES) and those spectra of known tetrahedral complexes is very striking. The band around 10,000 cm^{-1} is assigned to $^4A_2 \rightarrow {}^4T_1$ (F). The shoulder observed near 18,000 cm^{-1} is assigned to $^4A_2 \rightarrow {}^4T_1$ (P).[18] In some of the complexes both bands are split into two components. The splitting probably arises in each case from the less than perfect T_d symmetry that is anticipated for these materials. Bis(*N*-phenylsalicylaldiminato)cobalt(II) has been shown by spectral as well as crystallographic evidence to have a pseudotetrahedral geometry.[19,20] The electronic spectrum of this complex exhibits absorption bands at 7600, 10,700, 16,700 (sh), and 19,230 cm^{-1}. These band positions are in good agreement with those obtained for Co(XSALDAES)·nH$_2$O and also those obtained for *N,N'*-bis(salicylidene)polymethylenediaminocobalt(II) containing four to six methylene groups.[4] Since the spectra of hydrated and anhydrous Co(XSALDAES) are identical, it is most probable that a molecule of water is not coordinated to the metal in the solid state.

Absorption maxima from spectral measurements in chloroform are listed in Table III for some of the complexes. The similarity between solution and solid-state spectra is very striking which suggests that the tetrahedral geometry is maintained even in solution. Most of the complexes were also studied in *N,N*-dimethylformamide and similarly placed band maxima were found. As further evidence for a tetrahedral assignment, the intensities of the ν_2 and ν_3 bands are in the reported range for known tetrahedral complexes.[10,19]

By way of comparison the spectra of similar known five-coordinate, high-spin[21] and low-spin square-planar[10] cobalt(II) complexes are in disagreement with what we have observed for Co(XSALDAES).

The adoption of a pseudotetrahedral geometry instead of a square-planar or five-coordinate one as observed in the nickel(II) case supports the crystal field idea that for flexible polydentate ligands cobalt(II) forms more stable tetrahedral complexes than nickel(II). It also would appear from these results that the thioether linkage is insignificant concerning influencing the overall adopted structure. No doubt the low affinity of thioethers for first-row metals contributes to this observation although the restricting nature of the five-atom chain which contains the thioether group may prohibit a fifth coordination position to be spanned. The interaction of cobalt(II) with other dianionic pentadentate ligands is presently under way.

Registry No. Co(HSALDAES), 38402-75-4; Co(5-BrSALDAES), 38402-76-5; Co(5-CH$_3$SALDAES), 38402-77-6; Co[3-(CH$_3$)$_2$CHSALDAES], 38402-78-7; Co(5-NO$_2$SALDAES), 38402-79-8.

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Studies of an Acetylacetone Complex of Zinc Perchlorate

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In recent years several workers have reported the preparation of transition metal complexes of acetylacetone in which the ligand coordinates without the loss of a proton, *i.e.*, as an electrically neutral ligand instead of an anion. Allred and Thompson,[1] using several β-diketones, reported adducts with group IV tetrahalides, while van Leeuwen has prepared acetylacetone adducts of nickel(II)[2] and magnesium(II)[3] perchlorates. Sutin, *et al.*, has reported kinetic evidence for the complexation of transition metal ions by thenoyltrifluoroacetone[4] and by acetylacetone.[5] A group of Japanese workers has reported an adduct of acetylacetone with CoBr$_2$[6] as well as the crystal structures of both Mn(Hacac)$_2$Br$_2$[7,8] and Ni(acHac)$_2$Br$_2$.[9] The crystal structures, as well as infrared evidence, show that acetylacetone can coordinate to transition metal ions in either the keto or enol form in the solid state. In solution the kinetic studies,[4,5] as well as the nmr spectra reported by van Leeuwen[3] for [Mg(acHac)$_2$(H$_2$O)$_2$]$^{2+}$, show that both tautomers of the ligand are present. The nmr studies of Allred and Thompson[1] show only the keto form for Sn(acHac)Cl$_4$ in CH$_2$Cl$_2$, but ir studies indicate some dissociation of this complex in CH$_2$Cl$_2$. In order to investigate this type of complex further and in an attempt to determine the factors which influence the keto–enol tautomerism, we have prepared the new complex [Zn(acHac)$_2$(H$_2$O)](ClO$_4$)$_2$ and examined its nmr spectrum in CD$_3$NO$_2$.

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