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Substituted salen and baen Tetradentate Schiff-Base Ligands. Synthesis, Characterization, and Electrochemistry of Cobalt(III) Complexes

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Two series of Schiff bases were prepared by condensing either salicylaldehyde or benzoylacetaldehyde with methyl- or phenyl-substituted ethylenediamines in a 2:1 molar ratio. Synthetic procedures for the newly prepared ligands and improvements in preparation of previously characterized ligands are described. Polarographic studies on the tetradentate cobalt Schiff-base complexes of the form $[Co^{III}(SB)(C_5H_5N)_2]ClO_4$ indicate that groups in an axial conformation on the ethylene portion of the Schiff base interact with the pyridine molecules ligated to the axial sites on the metal ion, causing a positive shift in half-wave potentials. Despite the difference in structure between the two series of ligands, the axial influence is remarkably similar. The Co^{II}–Co^{I} couple is nearly insensitive to the structural changes.

Tetradentate Schiff-base (SB) complexes, particularly those of cobalt(II), have been of interest for several decades because of their general ability to form reversible adducts with molecular oxygen.[1] The dioxygen-binding ability of a Co(II) complex has been found to be enhanced[2,3] by increasing the electron density on the central metal ion through appropriate selection of the axial ligand trans to the dioxygen binding site or through substitutional variation of the tetradentate Schiff-base equatorial ligand. Polarographic and cyclic voltammetric half-wave potentials for the Co^{II}–Co^{III} couple have been used as a measure of the relative central-metal-ion electron density.[3,4] In more recent years, increasing attention has been placed on studying the relation between the spatial configuration of the Schiff-base chelate and the dioxygen-binding ability of the complex.[5-8]

These investigations, particularly with regard to dioxygen-binding complexes, have their basis in the hypothesis proposed by Vogt, Faigenbaum, and Wiberley[9] that the more easily oxidized the central metal ion in such complexes is, the better the complex will be at dioxygen-adduct formation. Further, these authors suggested that the electrode potential of the Co^{III}–Co^{II} couple could be adjusted by appropriate modification of the ligands. In order to investigate the validity of the hypothesis, it is useful to prepare a series of closely related Schiff-base chelates which may impart a sufficiently broad range of electrode potentials to the Co^{III}–Co^{II} couple.

The approach we have taken is to extend the work of Hanzlik et al.[8] by selecting as ligands those which are formed from salicylaldehyde or benzoylacetaldehyde and ethylenediamine or similar diamines and which generally have been referred to as salen and baen, respectively. In each series, modification by increasing methyl substitution on the bridging ethylene backbone has been made to observe the changes in the spectral and electrochemical behavior of the cobalt complexes and to ascertain the importance of these changes in the dioxygen-binding ability of the complexes. These changes are expected to be manifested as increasing steric hindrance of the axial binding sites of the cobalt complex, with a consequent ease of oxidation of the Co(II) and an increased ability to bind dioxygen.[3,8,10]

Synthesis and characterization of a number of previously unreported Schiff-base ligands as well as improvements in some previously described synthetic procedures are given here. Bis(pyridinato)cobalt(III) complexes of the ligands have also been prepared; preliminary electrochemical observations are reported and discussed.

Specific structures and the acronyms for the ligands are shown in Figure 1 and Table I. Full names for the compounds appear in the Experimental Section.

Results

Characteristic data on each ligand including the infrared, electronic, nuclear magnetic resonance, and mass spectra are included in the Experimental Section along with the synthetic procedures.

Table I. Structures and Acronyms of the Schiff Bases

ligand	R′	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
baenH_2[a]	H	H	H	H	H				
bammenH_2[b]	H	CH_3	H	H	H				
badmenH_2[b]	H	CH_3	CH_3	H	H				
batmenH_2[b]	H	CH_3	CH_3	CH_3	CH_3				
badpenH_2[b]	H	Ph	H	Ph	H				
dbmenH_2[c]	Ph	H	H	H	H				
salenH_2[d]						H	H	H	H
salmmenH_2[e]						CH_3	H	H	H
saldmenH_2[f]						CH_3	CH_3	H	H
saltmenH_2[b]						CH_3	CH_3	CH_3	CH_3

[a] See ref 11 and 12. [b] New Schiff base. [c] See ref 13. [d] See ref 4. [e] See ref 17 and 18. [f] See ref 12.

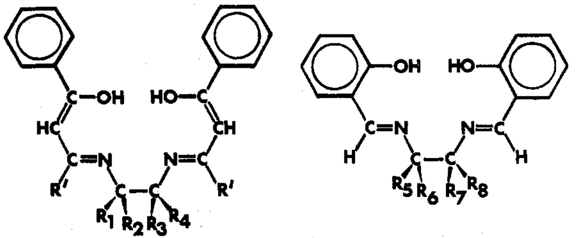

Figure 1.

Preliminary electrochemical data have been obtained in the form of half-wave potentials for the Co^{III}–Co^{II} and Co^{II}–Co^{I} Schiff-base couples and are given in Table II. The data were obtained at 0 °C in pyridine containing 0.1 mol L^{-1} tetraethylammonium perchlorate. On the basis of replicate determinations, the $E_{1/2}$ values are estimated to be accurate to within 5 mV. Within experimental error, all polarographic waves appear reversible and diffusion-controlled as confirmed by cyclic voltammetry at a hanging mercury drop electrode.

Discussion

Co^{III}–Co^{II} baen Complexes. In the baen–bammen–badmen–batmen series of complexes, the $E_{1/2}$ values for the Co^{III}–Co^{II} couple shift to more positive values as the degree of substitution on the ethylene backbone increases. The ease of reduction of Co(III) Schiff-base complexes has been described in terms of the relative extent of delocalization of electron density in the equatorial ligand plane.[3,4] As the electron density is increasingly delocalized from the central metal ion and the electron affinity of the "redox" orbital increases, the $E_{1/2}$ value for the Co^{III}–Co^{II} process should become more positive.

Since the basic structure of the equatorial ligand is the same throughout this series of complexes and any inductive effect

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Table II. Polarographic Half-Wave Potentials of $[Co(SB)(py)_2]ClO_4$ Complexes in Pyridine[a]

SB	$E_{1/2}$,[b] V	$E_{1/2}$,[c] V
baen	−0.532	−1.568
ba-(±)-mmen	−0.520	−1.570
badmen	−0.435	−1.584
batmen	−0.330	−1.595
ba-(±)-dpen	−0.470	−1.493
salen	−0.446	−1.428
sal-(±)-mmen	−0.434	−1.417
saldmen	−0.343	−1.430
saltmen	−0.225	−1.413
dbmen	−0.522	−1.566

[a] $E_{1/2}$ values reported vs. 1 M $AgNO_3(py)/Ag$ at 0 °C in 0.1 M tetraethylammonium perchlorate. Error is estimated to be less than ±5 mV. [b] For Co^{III}-Co^{II} process. [c] For Co^{II}-Co^{I} process.

due to increased methyl substitution should cause a negative $E_{1/2}$ shift, we suggest that the substituents cause a minor deformation of the plane of the equatorial ligand and an axial methyl–axial pyridine interaction. The resulting tetragonal distortion of the octahedral geometry of the complexes increases the electron affinity of the "redox" orbital.

In a report on the redox chemistry of cyclam (1,4,8,11-tetraazacyclotetradecane) and related macrocycles, Busch and co-workers[10] have suggested that the stabilization of nickel(II) over nickel(III) for *gem*-dimethyl substitution results from steric hindrance between the axial substituents and monodentate solvent molecules ligated to the central metal above and below the equatorial plane. The same observation was made for the stabilization of Co(II) with respect to Co(III).[19] In this case, the cobalt(III)–Schiff-base complex is expected to be octahedral in pyridine medium,[3,4] while the cobalt(II) complex is apparently five-coordinate, being a square-pyramidal molecule in the solid state.[20] The electrochemical data reported by Hanzlik et al.[8] indicate a release of one pyridine upon reduction of cobalt(III); and this relief of steric strain would tend toward a stabilization of the lower oxidation state.

Lovecchio et al.[10] have proposed an additive structural contribution for modifications to the cyclam ring. It was predicted that a $\Delta E_{1/2}(Co^{III}–Co^{II})$ value of +170 mV would result for each *two* axial methyl groups added to the macrocycle.[19] While derived for a rather different chelate, the prediction does semiquantitatively fit the behavior of the five-membered ring in the substituted baen complexes. We would conclude from our data that substitution of *one necessarily axial* group on the baen ethylene backbone stabilizes the Co(II) by ca. 100 mV.

Lovecchio et al.[10] further state that steric hindrance with the axially coordinated solvent (here, pyridine) would be exaggerated in the higher oxidation state since it would be expected that equilibrium metal–ligand distances would be shortened. It is not known what the equilibrium Co–N(py) distances are in these Co(III)–Schiff base complexes. The distance has been reported for the square-pyramidal Co(II) complexes as 210 pm in Co^{II}(salen)(py)[21] and 214 pm in Co^{II}(sal-(±)-bn)(py).[6] In both complexes, however, the cobalt atom has moved about 20 pm out of the Schiff-base plane toward the pyridine molecule.

The available structural data indicate that the Schiff-base plane is remarkably rigid in terms of Co–N and Co–O bond lengths, in spite of oxidation state changes of the central metal ion.[21] It is reasonable, then, to ascribe the effect of ethylenic substitutions to steric effects principally about the axial portions of the molecule, rather than deformation of the Schiff-base plane itself.

A three-term equation, linear in axial and equatorial distortion influences and logarithmic in inductive effect, has been found to fit the $E_{1/2}(Co^{III}–Co^{II})$ data for the baen series of complexes:

$$E_{1/2,\mathrm{substituted}} = E_{1/2,\mathrm{baen}} + 67A + 20D - 8 \log (10D) \qquad (1)$$

The numerical coefficients are expressed in mV, and A represents the number of *axial* methyl groups, while D represents the total number of methyl groups. Computed values of the half-wave potentials for the substituted baen complexes agree with the experimental values to within 1 mV. The interpretation of the terms of the equation as a large axial effect, a smaller equatorial distortion influence, and an even smaller inductive effect supports our conclusions.

Vicinal substitution of phenyl groups (trans) on the ethylene backbone (badpen) does not shift the $E_{1/2}$ as much as one axial methyl group (badmen) (+62 and +97 mV, respectively). Because of their bulky nature, the phenyls cannot adopt a truly equatorial conformation and some axial interaction is present.

Substitution of phenyl groups off the ethylene backbone (in dbmen) causes little $E_{1/2}$ shift. The ^1H NMR spectra (Me_2SO-d_6, Me_4Si) of the baen and dbmen complexes indicate the R′ phenyls (Figure 1) are rotated 90° to the plane of the benzoyl phenyls (the equatorial plane of the complex). In the dbmen complex, the ethylene protons are shifted 26 Hz upfield from the ethylene protons in the baen complex (δ 3.55 and 3.99, respectively), indicating the dbmen ethylene protons are above the plane of the R′ phenyls.[22] The methine protons in the dbmen complex are also shifted upfield compared with the methine protons in the baen complex (δ 5.86 and 5.92 (doublet center), respectively), indicative of the R′ phenyls being rotated 90° to the equatorial plane of the complex. Thus, the R′ phenyls cannot be considered as part of the delocalized π-electron system in the equatorial plane of the complex.

Co^{III}–Co^{II} salen Complexes. From Table II, we observe that one axial substituent (saldmen) results in a stabilization of Co(II) by about 100 mV and two axial substituents (saltmen) by about 200 mV, relative to the parent salen complex.

As with the baen series of complexes, an equation of the same form with slightly different coefficients fits the $E_{1/2}$ values for the Co^{III}–Co^{II} process:

$$E_{1/2,\mathrm{substituted}} = E_{1/2,\mathrm{salen}} + 69A + 27D - 15 \log (10D) \qquad (2)$$

The similarity with the effect for the baen series is remarkable, since the salen chelate would be expected to be more rigid than the baen chelate. Costa et al.,[4] on the basis of polarographic data, concluded that salen is a relatively weak electron donor to the cobalt compared to Schiff bases which are less likely to have an extensive π cloud to delocalize the electrons. The comparison between $E_{1/2}$ values (Co^{III}–Co^{II}) for baen and salen would lead us to the same conclusion, since baen does not stabilize Co(II) nearly as well as salen (by ca. 90 mV).

The $E_{1/2}$ shift for substitution of groups on the ethylene backbone has also been studied by Hanzlik et al.[8] Direct comparison of $E_{1/2}$ values between their report and ours cannot be made.[23] Intercomparison of data may be made by assuming the data sets to be internally consistent and calculating the $E_{1/2}$ shift relative to the unsubstituted salen complex.

Examination of both the Hanzlik et al. data[8] and ours shows a clustering generally into three groups in which (a) the substitution scarcely shifts the $E_{1/2}$ value (−5 to +15 mV), (b) a shift of +80 to +115 mV is found, and (c) a shift of +220 to +240 mV is observed. We therefore postulate that, in solution, complexes such as Co(sal-(±)-mmen), Co(sal-(±)-pen), Co(sal-(±)-bn), and Co(sal-(±)-chxn) are not exclusively in a conformation in which one substituent is axial, since they do not stabilize Co(II) as much as does the *gem*-dimethyl complex Co(saldmen). On the other hand, Co(sal-*ms*-chxn) necessarily is restricted to having one axial substituent, and less steric strain is apparently caused by adopting a Co(II) complex geometry for Co(sal-*ms*-bn) in which one methyl is axial than would be caused by both vicinal methyl groups adopting an eclipsed attitude.

The Co(saltmen) complex necessarily has two axial substituents, and the stabilization of the Co(II) is essentially doubled over that of group b.

Co(sal-(±)-dpen) adopts a middle ground, and the relaxation from an axial conformation may be more difficult than for Co(sal-(±)-bn).

If eq 2 is applied to predict the $E_{1/2}$ shift for the Co(sal-(±)-bn) and Co(sal-*ms*-bn) complexes studied by Hanzlik et al.,[8] the agreement with experimental data is good. For Co(sal-(±)-bn), $\Delta E_{1/2}$(exptl) = +15 mV and $\Delta E_{1/2}$(calcd) = +34 mV; for Co(sal-*ms*-bn), $\Delta E_{1/2}$(exptl) = +80 mV and $\Delta E_{1/2}$(calcd) = +103 mV. Part of the difference between the values must be attributed to a temperature effect, since the experimental data were obtained at 25 °C.

Co^{II}–Co^{I} Complexes. No simple correlation is evident between the $E_{1/2}$ shift for the Co^{II}–Co^{I} process and the nature of substitution. Our data for salmmen and saltmen both show a positive shift (stabilization of Co(I) over Co(II)) as do the Hanzlik et al.[8] data for the saldpen complex. However, all other salen derivatives show the opposite effect.

For the baen series, there is a stabilization of Co(II) over Co(I) as the degree of substitution increases. However, the substitution seems to have only a small effect.

Geometrically, the axial substitution argument is not particularly useful for the Co^{II}–Co^{I} process, inasmuch as the Co(I) complex (d^8) is probably square planar with no primary interaction with the pyridine molecules.[24] Therefore, steric crowding in the axial position is of less importance.

It must be noted that the Co^{II}–Co^{I} process may be complicated by a chemical reaction of the Co(I) complex with the supporting electrolyte, although the observations reported here indicate no such reaction occurs within the lifetime of the polarographic experiment, in agreement with a previous report.[25]

The steric crowding is certainly an oversimplification to use for arguing the trends in half-wave potentials with substitution on less than a totally rigid macrocyclic chelate. The distance between the central metal ion and the axial ligands would be expected to be quite sensitive to substitution on the ethylene backbone, and any elongation in this bond length would be expected to greatly affect the ligand field about the cobalt.[21,26]

Co^{III}–Co^{I} Transition. The difference in half-wave potentials between the Co^{III}–Co^{II} and the Co^{II}–Co^{I} processes has been reported for a series of trans tetraamine complexes of Co, Ni, and Cu,[27] and it was observed that the measure was nearly equal to the energy of the first d–d transition band for the different metal-ion complexes. In the complexes reported here, many show a half-wave potential difference of ca. 1 V, but the sal-*ms*-dpen and batmen complexes deviate from this by more than +200 mV. However, these complexes did not fall out of line with the structural arguments given earlier for the Co^{III}–Co^{II} complexes.

Conditions under which electrode-potential measurements for metal-ion complexes can reasonably be expected to correlate with spectral data have been presented by Vlcek.[28] Inasmuch as the coordination number of the cobalt center and the ligand field affecting its d energy levels are changing dramatically in going from d^6 Co(III) species to a d^8 Co(I) in the strongly coordinating pyridine medium, a simple correlation cannot be expected.[19]

Conclusion

From our preliminary electrochemical observations and those of others, we find that the salen and baen Schiff-base chelates do show a predictable relationship between structural modification and redox behavior but that relationship is not yet totally clear. The ability to control the redox behavior of the Schiff-base complex by alteration of structural features[9,28] is intriguing, since Carter et al.[3] have shown a linear relationship between the ability of such Co(II) complexes to be oxidized and their ability to form oxygen adducts, while Costa et al.[25] have also used the electrode potentials as a measure of Co(I) nucleophilicity in dealkylation reactions.

Experimental Section

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer using KBr disks and were calibrated with polystyrene film. NMR spectra were recorded on a Varian A-60 spectrometer. A suitable solvent was not found for badpenH_2. Deuterated solvents were purchased from Stohler Isotope Chemicals. Electronic spectra were recorded on a Cary 14 spectrophotometer using 1-cm quartz cells and anhydrous methanol as the solvent. High- and low-resolution mass spectra of the ligands were determined with an AEI Model 50-76 mass spectrometer equipped with a DS-30 data system. Electrochemical measurements were made with a multipurpose potentiostatic instrument[29] composed of Philbrick UPA-2 operational amplifiers. Polarograms were recorded on a Sargent Model SR recorder. The dropping mercury electrode had an open-circuit flow rate of 1.16 mg s^{-1} at a mercury column height of 50 cm and a drop time of 5.56 s. The jacketed cell used for electrochemical measurements was of our own design containing a platinum wire auxiliary electrode coiled around the working electrode. The reference electrode was made from a piece of Pyrex tubing (4 mm × 8 cm) sealed around a bead of soft glass at one end containing 1 mol L^{-1} $AgNO_3$ in pyridine and a 10-cm coil of Ag wire. Concentrations of complexes ranged from ca. 0.3 to 0.6 mmol L^{-1}. All measurements were made at 0 °C.

Reagents. Ethylenediamine, propylenediamine, 1,2-diamino-2-methylpropane, DL-isoamarine, and dibenzoylmethane were purchased from Aldrich Chemical Co. Salicylaldehyde was purchased from K & K Laboratories, Inc. 2,3-Diamino-2,3-dimethylbutane was prepared by the method of Sayre.[30] The slightly yellow product was used without further purification. Racemic 1,2-diamino-1,2-diphenylethane was prepared by a modification (see below) of the method of Lifschitz and Bos.[31] Benzoylacetaldehyde was obtained from the Cu(II) complex following the procedure of Buelow and Sicherer.[32] All solvents used in the syntheses were analytical grade reagents. Tetraethylammonium perchlorate (Eastman) was recrystallized four times from water and vacuum-oven-dried at 70 °C. Pyridine (Mallinckrodt or Fisher Scientific) was distilled from Zn and then BaO and was stored over Davison 3-Å molecular sieves. Elemental analyses were peformed by MicroTech Laboratories, Inc.

Preparation of 1,2-Diamino-1,2-diphenylethane. The Lifschitz and Bos[31] synthetic procedure was utilized with the following modification. The initial reaction to convert the isoamarine to the racemic *N*-acetyl-*N'*-benzoylstilbenediamine was lengthened from 3 to 6 h. Before filtering, more water was added to obtain a more quantitative precipitation. The product was filtered off and washed with 200 mL of boiling water.

The reaction time for the conversion to the dihydrochloride was changed to 24 h. After 14 h, one-third of the original amounts of alcohol and concentrated HCl were added because of gradual loss during refluxing. The stream of HCl gas was passed through the solution for the entire 24 h. The yield was ca. 90%.

The free amine was obtained from the dihydrochloride by using NaOH and Na metal in place of KOH and K metal. The strongly basic aqueous solution was filtered, and the crude product was allowed to air-dry. The crude amine was ground to a powder and extracted with 300 mL of ether in a Soxhlet extractor. Sodium metal was added to the ether solution and, after hydrogen evolution ceased, the solution was filtered. By use of a steam bath, the ether was distilled off until a small amount remained with the product. Dry nitrogen was passed through the flask to remove the last of the remaining ether from the diamine. The yield was 74%. The diamine was used without further purification.

Syntheses of the Schiff Bases. (Acronyms for the Schiff bases arise from considering the diamines as substituted ethylenediamines.)

baenH_2 = bis(benzoylacetaldehyde) ethylenediimine = 3,3'-(1,2-ethanediyldinitrilo)bis(propiophenone). Benzoylacetaldehyde (20 mmol) was diluted with ethanol (10 mL). Ethylenediamine (10 mmol) was diluted with ethanol (10 mL) and added dropwise to the rapidly stirring keto-aldehyde solution. The mixture was stirred for 2 h and then was evaporated to dryness. Two recrystallizations of the yellow solid from chlorobenzene gave nearly colorless crystals having a melting point of 144–146 °C. The yield was 61%. ^{1}H NMR (CH_2Cl_2, Me_4Si) (all J values in Hz): δ 3.41 (t, J = 3, 4 H), 5.72 (d, J = 7.5, 2 H), 6.68–7.10 (q, J = 13, 7.5, 2 H), 7.25–7.57 (m, 6 H), 7.75–8.00 (m, 4 H), 9.97–10.65 (br, s, 2 H). IR (strongest ten absorptions): 1630, 1582, 1557, 1492, 1477, 1318, 1269, 1210, 1055, 687 cm^{-1}. UV (λ_{max} in nm, log ϵ): 350, 4.53; 243, 4.27. Mass spectrum (molecular ion, base peak): 320, 160.

Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.92; H, 6.33; N, 8.79.

bammenH$_2$ = racemic bis(benzoylacetaldehyde) methylethylenediimine = racemic 3,3′-(1-methyl-1,2-ethanediyldinitrilo)bis(propiophenone). Racemic propylenediamine (10 mmol) was diluted with 10 mL of methanol and 5 mL of toluene and added dropwise to a rapidly stirring solution of benzoylacetaldehyde (20 mmol) dissolved in 15 mL of toluene. Nitrogen was passed over the solution until it became quite viscous. After the solution was stirred for 1 h, 10 mL of CCl_4 and 10 mL of ether were added to the yellow-orange solution. The stirring rate was increased and the impure ligand precipitated. The mixture was stirred for about 12 h and evaporated to dryness. The precipitate was boiled in 20 mL of ether and after cooling, the solid was filtered off. The light yellow crystals were dissolved in 10 mL of CCl_4 and the solution was filtered. Ether was then added to precipitate the ligand. After three crystallizations the nearly colorless crystals melted at 98–100 °C. The yield was 40%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.28 (d, J = 6.5, 3 H), 3.25 (m, 3 H), 5.67 (d, J = 7.5, 2 H), 6.58–7.07 (m, 2 H), 7.10–7.55 (m, 6 H), 7.65–7.95 (m, 4 H), 9.98–10.58 (br, s, 2 H). IR: 1640, 1600, 1588, 1551, 1501, 1479, 1270, 1250, 1230, 735 cm^{-1}. UV: 340, 4.51; 243, 4.25. Mass spectrum: 334, 174.

Anal. Calcd for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.33; H, 6.61; N, 8.27.

badmenH$_2$ = bis(benzoylacetaldehyde) 1,1-dimethylethylenediimine = 3,3′-(1,2-dimethyl-1,2-ethanediyldinitrilo)bis(propiophenone). Of all of the compounds reported, this Schiff base was the most troublesome to synthesize. Removal of impurities from the crude product was a tedious process. Benzoylacetaldehyde (20 mmol) was obtained from the copper salt as usual,[32] except in this case the sulfuric acid was cooled in an ice bath prior to the extraction. The ether solution of benzoylacetaldehyde (25 mL) was shaken with about 2 g of anhydrous sodium sulfate and filtered into the reaction vessel. The ether solution was cooled in a rock salt/ice bath, and most of the ether was evaporated with a stream of dry nitrogen. When the volume of the solution reached about 5 mL, 1,2-diamino-2-methylpropane (10 mmol) was added dropwise to the rapidly stirring keto-aldehyde over a period of 10 min. CCl_4 (10 mL) was added to the yellow solution and stirring was continued overnight while the solution warmed to room temperature. Evaporation of the solvent yielded an orange precipitate.

Anhydrous ethyl ether (15 mL) was added to the precipitate and after the mixture was stirred for a few minutes, it was cooled in an ice bath and the precipitate was filtered off. The precipitate was set aside and the filtrate was evaporated to dryness. CCl_4 (5 mL) was added to the residue and the mixture was warmed for a few minutes and decanted into a clean vessel, leaving a dark gummy residue behind. Hexane (5 mL) was added to the solution causing precipitation of more product. This dissolving, decanting, and reprecipitating procedure was repeated until most of the coloration was removed from the product. All of the precipitates were combined and dissolved in boiling ether/ethanol (5 mL/1 mL). After 30 min, more ether (2 mL) was added and the mixture was cooled with methanol/dry ice for 30 min. The nearly colorless precipitate was filtered and washed with dry ice cooled ether (20 mL). The product melted at 94–96 °C and was obtained in a 30% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.33 (s, 6 H), 3.05–3.31 (d, J = 7, 2 H), 5.60–5.85 (q, J = 7.5, 5, 2 H), 6.57–7.22 (m, 2 H), 7.25–7.58 (m, 6 H), 7.67–8.05 (m, 4 H), 10.28–10.87 (br, complex doublet, 2 H). IR: 1635, 1623, 1588, 1553, 1501, 1476, 1300, 1260, 1235, 726 cm^{-1}. UV: 356, 4.53; 337, 4.53; 245, 4.26. Mass spectrum: 348, 188.

Anal. Calcd for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.59; H, 6.86; N, 7.93.

batmenH$_2$ = bis(benzoylacetaldehyde) 1,1,2,2-tetramethylethylenediimine = 3,3′-(1,1,2,2-tetramethyl-1,2-ethanediyldinitrilo)bis(propiophenone). 2,3-Diamino-2,3-dimethylbutane (25 mmol) was added dropwise to a rapidly stirring solution of benzoylacetaldehyde (50 mmol) in 40 mL of ethanol/ether (1:1) cooled in an ice bath. After all of the amine had been added, the solution was removed from the ice bath and stirred overnight. The solvents were evaporated by blowing nitrogen over the solution. The crude product was recrystallized once from chloroform/1-propanol (ca. 1:1) and twice from chlorobenzene. The nearly colorless crystals melted at 196 °C. The yield was 60%. ^{1}H NMR (CD_3COCD_3, CCl_4, $CDCl_3$ (1:1.6:13), Me_4Si): δ 1.43 (s, 12 H), 5.77 (d, J = 7.5, 2 H), 6.88–7.27 (q, J = 13, 7, 2 H), 7.32–7.60 (m, 6 H), 7.83–8.07 (m, 4 H), 10.83–11.25 (br, d, J = 13, 2 H). IR: 1627, 1585, 1538, 1502, 1479, 1288, 1182, 1151, 728, 697 cm^{-1}. UV: 360, 4.55; 252, 4.27. Mass spectrum: 376, 188.

Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44. Found: C, 76.27; H, 7.33; N, 7.39.

Table III. Elemental Analytical Data for $[Co(SB)(py)_2]ClO_4$ Complexes

compd	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
$Co(baen)(py)_2ClO_4$	56.75	56.91	4.44	4.60	8.82	9.03
$Co(bammen)(py)_2ClO_4$	57.37	57.41	4.66	4.72	8.63	8.71
$Co(badmen)(py)_2ClO_4$	57.97	55.73	4.86	4.75	8.45	8.35
$Co(batmen)(py)_2ClO_4$	59.09	59.07	5.25	5.24	8.11	8.14
$Co(badpen)(py)_2ClO_4$	64.09	64.16	4.61	4.81	7.12	7.57
$Co(dbmen)(py)_2ClO_4$	64.09	63.39	4.61	4.59	7.12	7.02
$Co(salmmen)(py)_2ClO_4$	54.33	53.56	4.39	4.38	9.39	9.23
$Co(saldmen)(py)_2ClO_4$	55.05	54.99	4.62	4.62	9.17	9.16
$Co(saltmen)(py)_2ClO_4$	56.39	55.15	5.05	5.16	8.77	8.55

badpenH$_2$ = racemic bis(benzoylacetaldehyde) 1,2-diphenylethylenediimine = (±)-3,3′-(1,2-diphenyl-1,2-ethanediyldinitrilo)-bis(propiophenone). Racemic 1,2-diamino-1,2-diphenylethane (10 mmol) was dissolved in 20 mL of warm 2-propanol. Benzoylacetaldehyde (20 mmol) was diluted with 15 mL of methanol and added dropwise to the rapidly stirring amine solution. Precipitation began after about 20% of the keto-aldehyde had been added. After the addition was completed, the yellow solution was boiled for 10 min. The solution volume was reduced to about 20 mL by passing air over the warm mixture. The crude product was filtered off and washed with two 10-mL portions of ethyl ether. Two recrystallizations from toluene yielded nearly colorless crystals having a melting point of 195–196 °C. The yield was 60%. IR: 1640, 1586, 1538, 1498, 1479, 1302, 1284, 1236, 736, 689 cm^{-1}. UV: 341, 4.60; 250, 4.31. Mass spectrum: 472, 236.

Anal. Calcd for $C_{32}H_{28}N_2O_2$: C, 81.33; H, 5.97; N, 5.93. Found: C, 80.93; H, 5.96; N, 5.71.

dbmenH$_2$ = bis(dibenzoylmethane)ethylenediimine = 3,3′-(1,2-ethanediyldinitrilo)bis(3-phenylpropiophenone). Several attempts to condense dibenzoylmethane with ethylenediamine in alcoholic solutions were unsuccessful. Following a modification of the method of Carter et al.,[3] used for other diketone–ethylenediamine reactions, the desired compound was obtained. Dibenzoylmethane (20 mmol) and ethylenediamine (10 mmol) were added to 2-propanol (15 mL). While the solution was stirred, glacial acetic acid was added to adjust the pH to 6. The solution was refluxed for 1 h, and allowed to cool, and 1.63 g of product was filtered off. Another 0.3 g of ethylenediamine was added to the solution, the pH adjusted, and the solution refluxed for 1 h. Another 0.65 g of the product was obtained. A third adjustment of the pH and refluxing yielded another 0.1 g of dbmenH$_2$. The crude product was recrystallized twice from ethanol and twice more by dissolving the material in chloroform and precipitating the ligand by adding Skelly Solve B (bp 60–69 °C). The yield was about 50%. The nearly colorless crystals melted at 115 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.30 (t, J = 3, 4 H), 5.75 (s, 2 H), 7.12–7.57 (m, 16 H), 7.67–8.02 (m, 4 H), 11.27 (br, s, 2 H). IR: 1608, 1597, 1587, 1570, 1481, 1324, 1269, 751, 741, 690, 685 cm^{-1}. UV: 347, 4.57; 247, 4.34. Mass spectrum: 472.2116, 0.53%, 7 ppm; 236.1070, 100%, 2 ppm.

Anal. Calcd for $C_{32}H_{28}N_2O_2$: C, 81.33; H, 5.97; N, 5.93. Found: C, 80.61; H, 5.69; N, 5.91.

salmmenH$_2$ = sal-(±)-pn[18] = bis(salicylaldehyde) methylethylenediimine = (±)-2,2′-[(1-methyl-1,2-ethanediyl)bis(nitrilomethylidyne)]diphenol. After propylenediamine (10 mmol) was refluxed with salicylaldehyde (20 mmol) in ethanol (10 mL) for 18 h, evaporation of the solvent yielded ca. 5 mL of dark oil. Water (25 mL) was added and after the mixture was stirred and cooled in an ice bath, the aqueous layer was decanted. Hexanes (30 mL) were added to the oil and the mixture was boiled. The hot yellow solution

Table IV. Major Infrared Absorption Frequencies (cm^{-1}) of $[Co(SB)(py)_2]ClO_4$ Complexes[a]

ligand	frequency[b]													
salmmen	1624 vs	1604 vs	1537 s			1449 vs		1307 s	1133 s sh		1065 vs sh	762 s		695 s
saldmen	1620 vs	1605 vs	1535 s			1450 vs		1313 s	1128 s sh	1113 vs sh	1065 s sh	760 s	750 s	
saltmen		1603 vs	1537 s			1450 vs		1319 s	1144 vs			766 s		
baen		1608 vs		1509 vs	1480 vs	1453 vs	1402 vs		1122 s sh		1070 s sh		706 s	692 s
bammen		1608 vs		1507 vs	1484 vs	1451 vs	1405 vs	1386 s sh	1362 s		1075 s sh	761 s	706 s	695 s
badmen		1604 vs		1512 vs	1487 vs	1457 vs	1407 vs		1358 s	1121 s sh	1071 s sh	761 s		692 s
batmen		1596 s		1511 vs	1481 vs	1457 vs	1407 vs		1360 s	1138 s	1070 s sh			693 s
badpen		1600 vs	1582 s	1514 vs	1488 vs	1460 vs	1410 vs	1371 s	1361 s sh	1271 s	1072 s sh	762 s	709 s sh	698 vs
dbmen		1588 s	1567 s	1502 vs	1482 vs	1456 vs	1448 vs sh	1440 s sh	1410 vs	1119 s sh		760 s		695 vs

[a] The perchlorate absorptions at 1094 ± 2 and 620 ± 1 cm^{-1} have been excluded. [b] s = strong, v = very, sh = shoulder.

was decanted and the process was repeated using 20 mL and then 10 mL of hexanes. A stream of air evaporated the hexanes, and methanol (10 mL) was added to the yellow oil. After the solution was warmed, it was added to zinc acetate dihydrate (10 mmol) dissolved in 20 mL of hot 75% methanol. The zinc complex, presumably $Zn(salmmen)\cdot H_2O$,[33] precipitated from the yellow solution after a few minutes of heating and stirring. Water (35 mL) was added to the hot mixture and the yellowish solid was filtered off, washed with ether (4 × 15 mL), and air-dried. The light yellow product was obtained in a 70% yield. IR: 1638, 1600, 1539, 1471, 1444, 1391, 1337, 1298, 750, 733 cm^{-1}.

The zinc complex (2 mmol) was dissolved in hot methanol/pyridine (30 mL/5 mL). $Co(ClO_4)_2\cdot 6H_2O$ (2 mmol) was added, and after a few minutes, $HClO_4$ (2 mmol in 2 mL of H_2O) was added. After air was passed over the solution for 1 h, water (40 mL) and acetone (70 mL) were added to the dark brown solution. A stream of air reduced the solution volume to 25 mL, and the dark brown precipitate was filtered off. After the precipitate was washed with H_2O (10 mL) and ether (two 30-mL portions), it was redissolved in acetone (25 mL) and pyridine (10 mL) and heated to 55 °C for 1 h. The solution was filtered, water (30 mL) was added, and the volume was reduced to 25 mL. The precipitate was filtered off, washed with water (20 mL) and ether (three 15-mL portions), and air-dried. The yield was 76%.

saldmenH$_2$ = sal$_2$-*i*-bn[32] = bis(salicylaldehyde) 1,1-dimethylethylenediimine = 2,2′-[(1,1-dimethyl-1,2-ethanediyl)bis(nitrilomethylidyne)]diphenol. This Schiff base was made by a procedure very similar to that of Patel and Bailar.[34] This compound has been well characterized in the literature.[34-37] We obtained some additional electronic spectral data. UV–vis: 403, 3.25; 318, 3.87; 256, 4.35; 214, 4.65.

saltmenH$_2$ = bis(salicylaldehyde) 1,1,2,2-tetramethylethylenediimine = 2,2′-[(1,1,2,2-tetramethyl-1,2-ethanediyl)bis(nitrilomethylidyne)]diphenol. Salicylaldehyde (20 mmol) was diluted with 10 mL of methanol. 2,3-Diamino-2,3-dimethylbutane (10 mmol) was diluted with 6 mL of methanol and added dropwise to the rapidly stirring aldehyde solution. The solution was allowed to stand for several hours during which time precipitation of the product occurred. Two recrystallizations from methanol gave yellow needles with a melting point of 117 °C in a 62% yield. ^1H NMR ($CCl_4/CDCl_3$, 16:1, Me_4Si): δ 1.35 (s, 12 H), 6.58–7.36 (m, 8 H), 8.31 (s, 2 H), 13.53 (br, s, 2 H). IR: 1630, 1585, 1500, 1460, 1381, 1280, 1132, 1110, 827, 748. UV–vis: 402, 3.44; 317, 3.82; 256, 4.35; 214, 4.65. Mass spectrum: 324, 162.

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 73.85; H, 7.44; N, 8.71.

$[Co^{III}(SB)(py)_2]ClO_4$. Preparation of Complexes. Complexes of the Schiff bases were made by a modification of the procedure of Costa et al.[38] $Co^{II}(ClO_4)_2\cdot 6H_2O$ (5 mmol) was dissolved in 10–15 mL of methanol, and the Schiff base (5 mmol) was added to the stirring solution. Solid sodium hydroxide (5 mmol) was then added to the solution, and about a minute later, 3–5 mL of pyridine was added. Air was blown over or bubbled through the hot solution, and more methanol and pyridine were added to replace losses due to evaporation. After 2 or 3 h, the solution was allowed to evaporate to near dryness. Water (20–25 mL) was added while stirring was continued, and the brown precipitate was filtered off. The precipitate was washed with ether and redissolved in methanol/pyridine and then reprecipitated with water. After the solid was washed with ether, it was allowed to air-dry. The light brown powders were dissolved in hot pyridine or, for the saldmen complex, pyridine/acetonitrile (4:1), and ether was allowed to diffuse into the pyridine solution in a closed container. In 18–36 h, much larger dark brown crystals of the complexes were obtained by filtering off the lightly colored solvent and washing the solid with ether. The yields were about 90% in all cases. Elemental analytical data are given in Table III. IR data for the complexes are given in Table IV.

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Registry No. $[Co(baen)(py)_2]ClO_4$, 67891-28-5; $[Co(bammen)(py)_2]ClO_4$, 67891-30-9; $[Co(badmen)(py)_2]ClO_4$, 67891-32-1; $[Co(batmen)(py)_2]ClO_4$, 67891-34-3; $[Co(badpen)(py)_2]ClO_4$, 67891-36-5; $[Co(salen)(py)_2]ClO_4$, 32089-90-0; $[Co(salmmen)(py)_2]ClO_4$, 67891-38-7; $[Co(saldmen)(py)_2]ClO_4$, 67921-61-3; $[Co(saltmen)(py)_2]ClO_4$, 67891-40-1; $[Co(dbmen)(py)_2]ClO_4$, 67891-42-3; [Co(baen)(py)], 67891-43-4; [Co(bammen)(py)], 67891-44-5; [Co(badmen)(py)], 67891-45-6; [Co(batmen)(py)], 67891-46-7; [Co(badpen)(py)], 67891-47-8; [Co(salen)(py)], 30227-50-0; [Co(salmmen)(py)], 40784-79-0; [Co(saldmen)(py)], 63371-05-1; [Co(saltmen)(py)], 67891-48-9; [Co(dbmen)(py)], 67891-49-0; $[Co(baen)]^-$, 67891-50-3; $[Co(bammen)]^-$, 67891-51-4; $[Co(badman)]^-$, 67891-52-5; $[Co(batmen)]^-$, 67891-53-6; $[Co(badpen)]^-$, 67891-54-7; $[Co(salen)]^-$, 26220-77-9; $[Co(salmmen)]^-$, 67891-55-8; $[Co(saldmen)]^-$, 67891-56-9; $[Co(saltmen)]^-$, 67891-57-0; $[Co(dbmen)]^-$, 67891-58-1; baenH$_2$, 67891-07-0; bammenH$_2$, 67891-08-1; badmenH$_2$, 67891-09-2; batmenH$_2$, 67891-10-5; badpenH$_2$, 67891-11-6; dbmenH$_2$, 67891-12-7; salmmenH$_2$, 67920-91-6; saldmenH$_2$, 30180-37-1; saltmenH$_2$, 60306-02-7; benzoylacetaldehyde, 15397-33-8; ethylenediamine, 107-15-3; propylenediamine, 10424-38-1; 1,2-diamino-2-methylpropane, 811-93-8; 2,3-diamino-2,3-dimethylbutane, 20485-44-3; 1,2-diamino-1,2-diphenylethane, 16635-95-3; dibenzoylmethane, 120-46-7; salicylaldehyde, 90-02-8; $Zn(salmmen)\cdot H_2O$, 18177-50-9.

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Coordination Chemistry of Microbial Iron Transport Compounds. 15.[1] Electrochemistry and Magnetic Susceptibility of Iron(III)–Hydroxamate and –Thiohydroxamate Complexes

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The electrochemical reduction of hydrox*a*mate and thiohydrox*a*mate complexes of ferric ion as well as the corresponding hydrox*i*mate complexes has been examined by cyclic voltammetry on hanging mercury drop electrodes. In all cases the ferric complexes have been found to undergo reversible or quasi-reversible reductions under suitable conditions. Deprotonating the hydroxamato complexes stabilizes the Fe(III) vs. the Fe(II) state, while replacing the carbonyl oxygen by sulfur stabilizes the Fe(II) vs. the Fe(III) state. This makes biological iron release by reduction even easier for thiohydroxamate than for hydroxamate siderophores. The magnetic susceptibilities of tris(thiobenzohydrox*a*mato)iron(III) as well as the tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydrox*i*mato)iron(III) have been measured over the temperature range 5–71 K. Contrary to previous reports, there is no evidence of spin crossover. The ferric thiohydrox*a*mato and thiohydrox*i*mato complexes obey Curie–Weiss ($\chi = C/(T - \Theta)$, $\Theta = -3$ K) and Curie laws, respectively, in this temperature range and contain high-spin iron(III) with magnetic moments of ~5.4 μ_B.

Introduction

The siderophores are low-molecular-weight compounds which are manufactured by microbes to facilitate uptake of ferric iron. The insolubility of ferric hydroxide at physiological pH and the essential nature of iron for microbial growth apparently engendered the production of a wide range of powerful sequestering agents for ferric ion—the siderophores. The general properties of these agents[2,3] and the role of iron in microbial physiology[4] have been the subjects of recent reviews. The functional groups in these siderophores are the hydroxamate and catecholate bidentate chelating groups as found in ferrichromes,[5] ferrioxamines,[6] and enterobactin.[7] Recently cupric and ferric complexes of *N*-methylthioformhydroxamic acid have been isolated from culture broths of *Pseudomonas fluorescens*;[8,9] however, the function of these complexes is not fully understood.

As part of our interest in siderophore electrochemistry, we previously examined the cyclic voltammetric behavior of ferric hydroxamate complexes in comparison with that of ferric enterobactin, a naturally occurring catechol-based siderophore.[10] The only previous report of ferric hydroxamate electrochemistry was that of Keller-Schierlein and co-workers in 1960.[11] Our studies were performed to clarify the iron release mechanism from siderophores, which is thought to occur via reduction of Fe(III) to the weakly bound Fe(II) state. We have subsequently extended these studies to the ferric thiohydroxamate system in order to determine the effect of thio substitution on the electrochemical behavior of the siderophores and to examine the possible role reduction plays in iron release from thiohydroxamate siderophores.

Recently Murray et al.[12] reported the variable-temperature magnetic susceptibility data for some ferric tris(thiobenzohydroxamato) complexes. They found that these complexes display spin-crossing behavior in the temperature range ~100–300 K. In contrast, we report here variable-temperature magnetic susceptibility data for such compounds in the temperature range ~5–71 K, which show Curie or Curie–Weiss behavior with no indication of spin-crossover behavior. The compounds studied include tris(thiobenzohydroxamato)iron(III) and the tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydroximato)ferrate(III). We also describe the electrochemical behavior of the ferric complexes of *N*-methylbenzohydroxamate, its thio analogue *N*-methylthiobenzohydroxamate, acetohydroxamate, and the N-deprotonated hydroxamates.

Experimental Section

Synthesis of Compounds. Tris(acethydroxamato)iron(III), tris(benzohydroxamato)iron(III), tris(thiobenzohydroxamato)iron(III), tris(*N*-methylbenzohydroxamato)iron(III), and tris(*N*-methylthiobenzohydroxamato)iron(III) were prepared by literature methods.[13-15] Sodium tris(benzohydroximato)ferrate was prepared from sodium hydroxide and the corresponding hydroxamato complex[15] and was recrystallized from water; $[Co(en)_3][Fe(PhC(S){=}N(O))_3]$ was prepared from $[Co(en)_3]I_3$ and potassium tris(thiobenzohydroximato)ferrate as reported eariler and gave satisfactory elemental analyses.[16]

Physical Measurements. Electrochemical measurements were performed using the three-electrode configuration. Triangular waves were generated by the Princeton Applied Research (PAR) 175

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