Formation of a substituted pyridine from diethyl oxaloacetate is then difficult to understand, since, unlike the comparison of DMAD and biacetyl reactants, the alternative cyclization steps for methyl vinyl ketone and diethyl oxaloacetate are equivalent. A possible explanation of the results may lie in differences in conformational flexibility of the N-alkylated intermediates, though another possibility is that the diethyl oxaloacetate reaction actually involves C alkylation as its initial step (Scheme VIII).

A final, less perplexing, anomaly is the lack of importance of carbanion addition in the diethyl oxaloacetate reaction compared to that of acetylacetone. This may simply be a reflection of the fact that the enolate anion from diethyl oxaloacetate is a weaker base, and hence a poorer nucleophile, than that from acetylacetone.

While strategies for the selective and controlled utilization of coordinated imine reactivity required further clarification,[40] it is quite apparent that all possible reaction sites identified in basic studies may be exploited in facile syntheses of complex organic molecules. Further, these organic products may be species difficult to isolate or unstable in their uncoordinated form. Their generation therefore offers the prospect of increasingly more sophisticated syntheses at metal ion centers.

Supplementary Material Available: Tables SUP-1, SUP-3, and SUP-4, containing solution and refinement procedures, anisotropic thermal parameters, and least-squares planes, and Figure SUP-1, showing a stereodiagram of the unit cell structure of the complex iodide (5 pages); Table SUP-2, listing structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

(39) Myers, J. F.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1238 and references therein.

(40) Study of several closely related systems has, for example, shown that steric factors and more subtle aspects of ligand acidity enhancement can be well important: Engelhardt, L. M.; Gainsford, A. R.; Gainsford, G. J.; Golding, B. T.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 4551-4563 and references therein.

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Oxidation of the Bis(1,2-ethanediamine)(sarcosinato)cobalt(III) Ion with Thionyl Chloride

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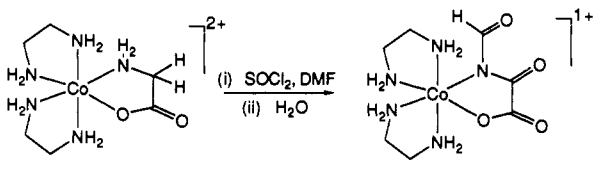
The oxidation of bis(1,2-ethanediamine)(sarcosinato)cobalt(III) ion with $SOCl_2$ in dimethylformamide gave the *N*-methylthiooxamato complex as the final product. The results, along with others, implicate the acid chloride chelate, a sulfine, and the methyl thiooxamato chelate as intermediates en route. The thiooxamato sulfur atom retains a nucleophilic capability and adds readily to cyclohexene in the thionyl chloride–dmf reaction medium to give an unusual imido hydroxycyclohexane thioester complex. Various results, including those in this paper, indicate that the chelated acid chloride readily loses an α-carbon proton and the resulting carbanion captures $SOCl^+$. Elimination of HCl yields the sulfine and further addition of $SOCl^+$, eliminations, and rearrangement yield chelated thiooxamate, which reacts even further under the pseudo-Vilsmeier conditions to the *N*-methyloxamato chelate complex.

Introduction

Previously, the oxidation of a variety of α-amino acidato complexes containing tertiary α-carbon centers with $SOCl_2$ in dimethyl formamide (dmf) to give the corresponding α-imino acidato complexes has been described.[1] That work was undertaken partly in order to shed some light on the path by which the glycinato complex **1** reacts with $SOCl_2$ in dmf to give the *N*-formyloxamato complex **2** and partly to synthesize new imino acid complexes.



(1) (2)

Bidentate, N,O-attachment of an α-amino acid to a metal center such as cobalt(III) serves to protect the ligating groups and to activate the proton(s) on the α-carbon atom. Coordination of the amine gives the nitrogen atom some ammonium ion character, and in addition, the metal-bound carboxylate ion has some ester character. These two features, together with the higher positive charge of the complex overall, combine to activate the proton(s) on the adjacent carbon atom[2,3] and thereby to facilitate carbanion formation. A mechanism for the formation of the α-imino acidato complexes (Scheme I) was proposed,[1] which involved, initially, the formation of the more highly activated chelated α-amino acid chloride and then deprotonation at the α-carbon center. Reaction of the resulting carbanion with $SOCl_2$ gave the α-sulfinyl chloride. Subsequent extrusion of sulfur monoxide and hydrolysis produced the α-imino acidato products. However, the presence of an additional proton on the secondary α-carbon center of the glycinato complex instead of an alkyl substituent allows an alternative path by which the α-sulfinyl chloride species **3** may react (Scheme I, R = H). Loss of the second α-proton and the chloride ion from this molecule would give the chelated sulfine **4**. Thus, it was concluded that the α-amino acidato complexes containing tertiary α-carbon centers could behave differently from the glycinato complex **1**. The sarcosinato complex **5** was therefore employed as an analogue for the study of these oxidation routes. While this complex is structurally similar to the glycinato complex **1**, it was hoped that it would be sufficiently different to allow the isolation or characterization of intermediates, without differing with respect to the mechanism of reaction. Also, the presence of the methyl group on the amine nitrogen atom should prevent the formylation reaction. Any activation of the system resulting from formylation would then be lost, and the intermediates along the reaction path might prove stable enough to be isolated.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in D_2O with a Jeol JNM-FX 200 Fourier transform spectrometer, using sodium 3-(trimethylsilyl)-

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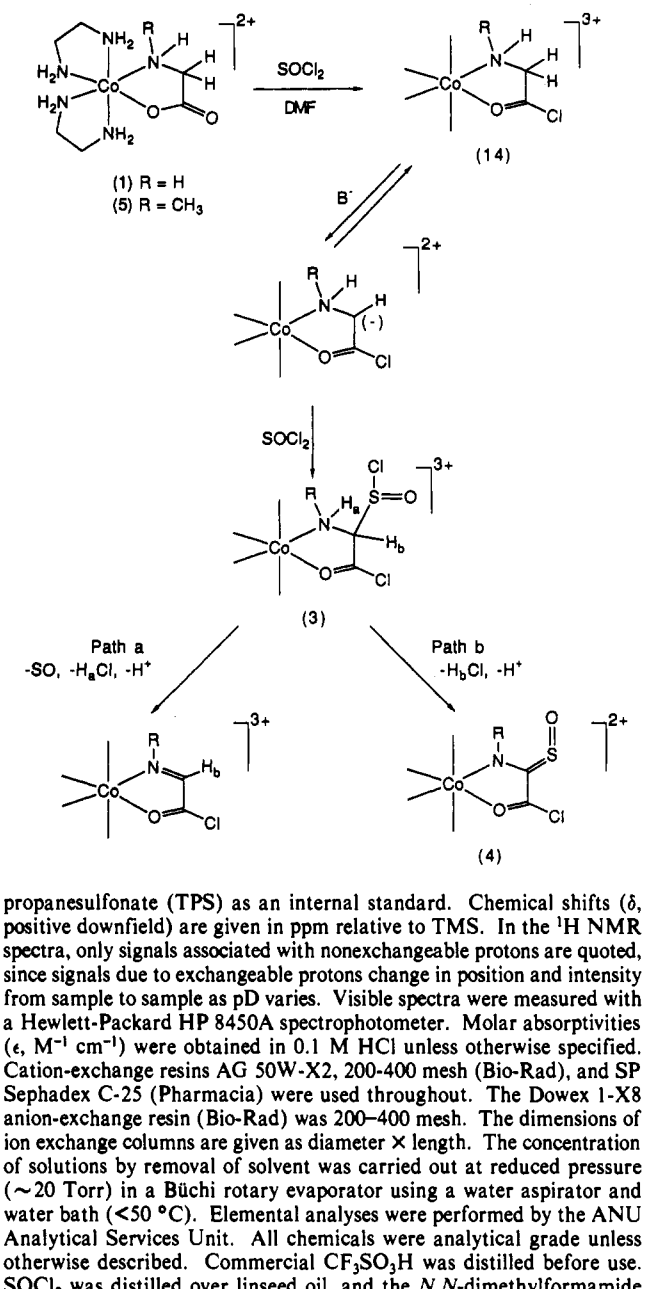
(1) Hammershøi, A.; Hartshorn, R. M.; Sargeson, A. M. *Inorg. Chem.* **1990**, *29*, 4525 and references therein.
(2) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133.
(3) Williams, D. H.; Busch, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 4644.

0020-1669/91/1330-1800$02.50/0

Scheme I



propanesulfonate (TPS) as an internal standard. Chemical shifts (δ, positive downfield) are given in ppm relative to TMS. In the ^1H NMR spectra, only signals associated with nonexchangeable protons are quoted, since signals due to exchangeable protons change in position and intensity from sample to sample as pD varies. Visible spectra were measured with a Hewlett-Packard HP 8450A spectrophotometer. Molar absorptivities (ϵ, M^{-1} cm^{-1}) were obtained in 0.1 M HCl unless otherwise specified. Cation-exchange resins AG 50W-X2, 200-400 mesh (Bio-Rad), and SP Sephadex C-25 (Pharmacia) were used throughout. The Dowex 1-X8 anion-exchange resin (Bio-Rad) was 200–400 mesh. The dimensions of ion exchange columns are given as diameter × length. The concentration of solutions by removal of solvent was carried out at reduced pressure (~20 Torr) in a Büchi rotary evaporator using a water aspirator and water bath (<50 °C). Elemental analyses were performed by the ANU Analytical Services Unit. All chemicals were analytical grade unless otherwise described. Commercial CF_3SO_3H was distilled before use. $SOCl_2$ was distilled over linseed oil, and the *N,N*-dimethylformamide (dmf) and dimethyl sulfoxide (dmso) were dried over 3-Å molecular sieves.

$[Co(en)_2(sar)](CF_3SO_3)_2\cdot H_2O\cdot 0.5CF_3SO_3H$ (5) (en = 1,2-Ethanediamine). $[Co(en)_2(OH)(OH_2)](ClO_4)_2$ (30 g) was dissolved in DMSO (100 mL). Sarcosine (6.54 g) was added and the solution heated for 1 h at 80 °C. After being cooled to room temperature, the reaction mixture was diluted with H_2O (5 L) and adsorbed on a column of AG 50W-X2 resin (7.5 × 20 cm). The column was thoroughly washed with H_2O (5 L) and then eluted with 1 M HCl. Several minor purple and red bands moved down the column ahead of the major red band, which was collected and taken to dryness before the solid was dissolved in warm 3 M HCl (75 mL). Ethanol was added to the point of turbidity and the solution heated on a steam bath until it cleared. Crystals of $[Co(en)_2(sar)]Cl_2$ deposited on cooling to 20 °C, after which time storage in the freezer produced a large amount of the salt as a red powder. This was collected and washed with ethanol and diethyl ether. The air-dried powder was then dissolved in the minimum volume of CF_3SO_3H and dry nitrogen bubbled through the solution for 2 h. The crude product was precipitated by slow addition of this solution to a large volume of diethyl ether, collected, and immediately redissolved in acetonitrile. Cooling in the freezer gave the slightly hygroscopic trifluoromethanesulfonate salt **5**. Anal. Calcd for $CoC_9H_{22}N_5O_8S_2F_6\cdot H_2O\cdot 0.5CF_3SO_3H$: Co, 8.96; C, 17.34; H, 3.68; N, 10.65; S, 12.18; F, 21.66. Found: Co, 9.0; C, 17.5; H, 3.8; N, 10.6; S, 12.0; F, 21.3. ^1H NMR (of the chelated amino acid): 3.85, 3.47 (AB, J_{AB} = 17.6 Hz) (α-methylene); 2.51 (s) ($N-CH_3$).

$[Co(en)_2(gly)](CF_3SO_3)_2\cdot CF_3SO_3H$ (1) was prepared according to the method of Curtis et al.[4] except that the racemic complex was used in the preparation of the trifluoromethanesulfonate salt.

$[Co(en)_2(N(CH_3)CSCO_2)]Cl\cdot H_2O$ (6). $[Co(en)_2(sar)](CF_3SO_3)_2\cdot H_2O\cdot 0.5CF_3SO_3H$ (5) (1 g) was dissolved in dmf (5 mL), the solution was cooled in an ice–salt bath, and $SOCl_2$ (1 mL) was added dropwise. A precipitate formed, and further $SOCl_2$ (1 mL) was added after 1 min. The precipitate slowly redissolved, and the reaction mixture was stirred for 10 min out of the cooling bath. The reaction was quenched by addition to H_2O (1 L), with no precipitate of sulfur being formed, and the solution adsorbed on a Sephadex column (4 × 10 cm). After washing with H_2O, a single orange band was eluted with 0.025 M $NaClO_4$. The eluate was adsorbed on AG 50W-X2 resin (4 × 10 cm), and after washing with 0.25 M HCl the major orange band was eluted with 0.5 M HCl. The complex should not be left on AG 50W-X2 resin any longer than necessary, as it decomposes slowly in acid media. The eluate was taken to dryness, and the resulting oil solidified on trituration with H_2O. The solid was collected, washed with ethanol and diethyl ether, and air-dried to give the *N*-methylthiooxamato complex **6** (0.41 g, 77%). Anal. Calcd for $CoC_7H_{19}N_5O_2SCl\cdot H_2O$: Co, 16.85; C, 24.04; H, 6.05; N, 20.03; S, 9.17; Cl, 10.14. Found (with C, H, and N analyses for a second sample): Co, 16.9; C, 24.0; H, 5.8; N, 20.0; S, 8.8; Cl, 10.5. IR (C=S): 1100, 1395, 1494 cm^{-1}. Visible spectrum (λ (nm), $\epsilon)_{max}$ in H_2O: 488, 189. ^1H NMR: 2.6–3.0 (br) (en methylenes); 3.39 (br) ($N-CH_3$). In some preparations a further, minor, red band was obtained on elution with 4 M HCl. This product has been tentatively identified as the dimer complex **7** and can be obtained in higher yield when longer reaction times are used as described below.

$[Co(en)_2(N(CH_3)CSCO_2)]O_3SCF_3$. $[Co(en)_2(N(CH_3)CSCO_2)]Cl\cdot H_2O$ (0.1 g) was dissolved in as little water as possible (ca. 10 mL), and ca. 1 g of $NaO_3SCF_3\cdot H_2O$ was added. Over night crystals formed, which were collected and washed with ethanol and ether. Anal. Calcd for $CoC_8H_{19}N_5O_5S_2F_3$: Co, 13.23; C, 21.58; H, 4.30; N, 15.73; F, 12.80; S, 14.40. Found: Co, 13.68; C, 21.51; H, 4.5; N, 15.61; F, 13.0; S, 14.2.

Sulfur(VI) Production in Synthesis of $[Co(en)_2(N(CH_3)CSCO_2)]Cl\cdot H_2O$ (6). $[Co(en)_2(sar)](CF_3SO_3)_2\cdot H_2O\cdot 0.5CF_3SO_3H$ (5) (0.895 g) was dissolved in dmf (10 mL). The solution was cooled in an ice–salt bath, and $SOCl_2$ (1 mL) was added. After the mixture was stirred for 10 min, the reaction was quenched by addition to H_2O (100 mL). The resulting solution was acidifed with HCl (5 mL) and $BaCl_2$ (1 g) added. A white precipitate of $BaSO_4$ formed immediately. This suspension was digested on a steam bath for 20 min before being filtered on a fine glass frit of known mass. After being dried overnight at 90 °C, the frit was weighed, with the weight of $BaSO_4$ = 0.223 g, 70% of the theoretical amount of sulfur(VI), assuming quantitative conversion of the sarcosinato complex to the *N*-methylthiooxamato complex **6** (sulfur(II)). A blank experiment in which the complex was omitted gave no $BaSO_4$.

$[Co(en)_2(N(CH_3)COCO_2)]PF_6\cdot 2H_2O$ (8). $[Co(en)_2(N(CH_3)CSCO_2)]Cl\cdot H_2O$ (6) (0.5 g) was suspended in H_2O (20 mL). Most of the complex dissolved on stirring. H_2O_2 (30%) (1.5 mL) was added, and the remaining solid redissolved. The solution darkened and then turned orange as sulfur precipitated out. The precipitate was removed by filtration and the filtrate adsorbed on a short AG 50W-X2 column (4 × 4 cm). The column was washed with H_2O (500 mL), and the single red band was eluted with 0.5–1 M HCl. There was some decomposed product on the top of the column. The HCl eluate was taken to dryness, and then the solid was redissolved in the minimum volume of H_2O. The complex was crystallized by the addition of small amounts of NH_4PF_6. The solid was collected, washed with ethanol and diethyl ether, and air-dried to yield the *N*-methyloxamato complex **8**. Anal. Calcd for $CoC_7H_{19}N_5O_3PF_6\cdot 2H_2O$: Co, 12.78; C, 18.23; H, 5.03; N, 15.19; P, 6.72; F, 24.72. Found: Co, 13.0; C, 18.1; H, 4.9; N, 14.8; P, 6.8; F, 24.5. Visible spectrum (λ (nm), $\epsilon)_{max}$: 492, 148. ^1H NMR: 2.6–3.0 (br) (en methylenes); 3.01 (s) ($N-CH_3$). ^{13}C NMR: 33.1 ($N-CH_3$); 44.4, 45.3, 45.7, 46.6 (en methylenes); 163.7 (Co—N—C=O); 169.9 (Co—O—C=O).

Longer Term Reaction of $[Co(en)_2(sar)](CF_3SO_3)_2\cdot H_2O\cdot 0.5CF_3SO_3H$ (5) with $SOCl_2$. $[Co(en)_2(sar)](CF_3SO_2)_2\cdot H_2O\cdot 0.5CF_3SO_3H$ (5) (1 g) was dissolved in dmf (8 mL). $SOCl_2$ (1.5 mL) was added dropwise and the reaction vessel placed in a water bath. A red precipitate formed immediately and then slowly turned orange as the stirring continued. After 3 h, the precipitate had redissolved. Stirring was continued for a further 15 h before the reaction was quenched by addition to H_2O (1 L). The solution was stirred for 15 min, filtered to remove the sulfur, and then adsorbed on an AG 50W-X2 column (5 × 10 cm). After thorough washing with H_2O, the column was eluted with 1 M HCl, revealing four

(4) Curtis, N. J.; Hammershøi, A.; Nicolas, L. M.; Sargeson, A. M.; Watson, K. J. *Acta Chem. Scand., Ser. A* **1987**, *41*, 36.

orange-red bands, which were eluted and taken to dryness. Fraction 1 gave ~0.3 g of solid material. A significant amount of this material was an organic impurity that had a ^{1}H NMR spectrum containing three singlets at 3.19, 3.30, and 7.59 (integral ratio 3:3:1). The complex (**9**) could be obtained in pure form by recrystallization from hot H_2O but has not been identified as yet. Anal. Calcd for $CoC_7H_{19}N_5O_5SCl\cdot2.5H_2O$: C, 19.80; H, 5.69; N, 16.49; S, 7.55; Cl, 8.35. Found: C, 19.7; H, 5.5; N, 16.3; S, 7.6; Cl, 8.5. Visible spectrum (λ (nm), $\epsilon)_{max}$: 486, 128. ^{1}H NMR: 2.6–3.0 (br) (en methylenes); 3.96 (s) (N–CH_3). ^{13}C NMR: 44.1, 44.2, 44.5, 44.6, 45.4, 46.0, 46.2 (en methylenes and N–CH_3); 169.5, 175.0 (C—N=C, C—O—C=O). In aqueous solution this complex slowly converted into the *N*-methyloxamato complex **8**. Fraction 2 gave ~0.1 g of a compound that was identified by its ^{1}H NMR spectrum as mostly the *N*-methylthiooxamato complex **6**. There was an indication of a brownish compound that eluted with this band; in some experiments the band gave the appearance of being split into two bands. The *N*-methylthiooxamato chloride complex **6** was readily isolable in pure form as a result of its low solubility in H_2O and could be crystallized from both fractions. Fraction 3 gave ~0.1 g of a complex that was identified by its ^{1}H NMR and ^{13}C NMR spectra as the *N*-methyloxamato complex **8**. Fraction 4 was eluted with 4 M HCl and gave ~0.1 g of an oily residue. This residue was taken up in the minimum volume of H_2O and precipitated by addition to ethanol (50 mL). After digestion on a steam bath for 4 h, the precipitate was collected, washed with ethanol and diethyl ether, and dried in vacuo for 48 h to yield the dimer complex **7**. Anal. Calcd for $Co_2C_{14}H_{40}N_{10}O_3SCl_4\cdot4H_2O$: C, 21.28; H, 5.87; N, 17.72; S, 4.06; Cl, 17.94. Found: C, 21.5; H, 6.2; N, 17.7; S, 3.9; Cl, 18.0. Visible spectrum (λ (nm), $\epsilon)_{max}$: 480, 245. ^{1}H NMR: 2.6–3.0 (br) (en methylenes); 3.79 (s) (N–CH_3). ^{13}C NMR: 44.8, 45.6, 46.8, 47.0 (en methylenes; in some spectra the signals at 44.8 and 47.0 exhibited a slight splitting); 45.0 (N–CH_3); 169.7, 171.5 (Co—N=C—S, Co—O—C=O). The yields of these reactions were quite variable. In general terms, experiments over shorter reaction times gave more of the *N*-methylthiooxamato complex **6** (fraction 2) and less of fraction 1 and the dimer complex **7** and very little if any of the oxamato complex **8** (fraction 3). Longer reaction times gave more of fraction 1, less of fraction 2, and small amounts of fraction 3, and the amount of dimer **7** (fraction 4) remained constant at about 15% by weight of the isolated products.

Treatment of $[Co(en)_2(N(CH_3)CSCO_2)]^+$ (6) with $SOCl_2$. $[Co(en)_2(N(CH_3)CSCO_2)]Cl\cdot H_2O$ (**6**) (0.48 g) was converted to the trifluoromethanesulfonate salt by passing it down a column of Dowex 1-X8 anion-exchange resin (4 × 10 cm) in the trifluoromethanesulfonate form. The eluate was taken to dryness, and the solid was then suspended in dmf (20 mL). $SOCl_2$ (2 mL) was added dropwise to the solution whereupon an orange precipitate formed in addition to the remaining solid material. After 30 min, the precipitate and the remaining starting material had dissolved. The reaction mixture was stirred for a further 4 h before being quenched by addition to H_2O (1 L) and adsorbed on a column of AG 50W-X2 resin (4 × 10 cm). There was some green decomposition product evident on the top of the column. Elution with 1 M HCl gave rise to four bands similar to those described in the long-term treatment of the sarcosinato complex **5** with $SOCl_2$. Comparison of the ^{1}H NMR spectra of fractions 1 and 2 and both ^{1}H and ^{13}C NMR spectra of bands 3 and 4 with those of the sarcosinato experiment confirmed that the products from this reaction were the same.

$[Co(en)_2(N(CH_3)=C(SC_6H_{10}OH)CO_2)]Cl_2\cdot0.5HCl\cdot H_2O$ (10) and $[Co(en)_2(N(CH_3)=C(SC_6H_{10}Cl)CO_2)]Cl_2\cdot0.5H_2O$ (11). $[Co(en)_2(sar)](CF_3SO_3)_2\cdot H_2O\cdot0.5CF_3SO_3H$ (**5**) (2 g) was dissolved in dmf (15 mL). Cyclohexene (1 mL) was added, followed by $SOCl_2$ (2 mL), and the reaction flask cooled in an ice bath as the reaction rapidly heated up to boiling point. After 5 min, chloroform (30 mL) was added to the reaction mixture, followed by H_2O (60 mL). The aqueous layer was separated and the chloroform layer extracted a further three times with H_2O (50 mL). The combined aqueous layers were diluted with H_2O (750 mL) and adsorbed on AG 50W-X2 resin (4 × 12 cm). The column was washed with H_2O (500 mL) and then eluted with 1 M HCl to reveal two orange-red bands. The first fraction was eluted and taken to dryness. Trituration with ethanol gave a red solid, which was collected and washed with ethanol and diethyl ether. Drying in vacuo for 24 h gave the 2-hydroxycyclohexyl *N*-methylthiooximidate ester complex **10** (0.55 g). Anal. Calcd for $CoC_{13}H_{30}N_5O_3SCl_2\cdot0.5HCl\cdot H_2O$: Co, 11.73; C, 31.07; H, 6.52; N, 13.94; S, 6.38; Cl, 17.64. Found: Co, 11.8; C, 30.9; H, 6.4; N, 13.7; S, 6.1; Cl, 16.8. Visible spectrum (λ (nm), $\epsilon)_{max}$: 484, 140. ^{1}H NMR: 1.2–2.3 (br), (cyclohexane methylenes); 2.6–3.0 (br) (en methylenes); 3.4 (m), 3.1 (m) (CHOH, diastereoisomers); 3.51 (s), 3.59 (s) (N–CH_3, diastereoisomers); 4.45 (m), (CH–S–). ^{13}C NMR (mixture of diastereoisomers): 23.7, 23.7, 26.0, 26.0, 32.6, 33.0, 35.7, 35.7, (cyclohexane methylenes); 42.6, 43.0 (N–CH_3); 44.45, 44.55, 45.3, 45.3, 45.9, 45.9, 46.6, 46.7 (en methylenes); 54.8, 55.3 (CH–S–); 75.1, 75.7 (CH-OH); 170.5, 170.7 (C—N=C—S); 179.8 (Co—O—C=O). The second fraction was treated in a manner similar to that of the first to yield the 2-chlorocyclohexyl *N*-methylthiooximidate ester complex **11** (1.0 g). Anal. Calcd for $CoC_{13}H_{29}N_5O_2SCl_3\cdot0.5H_2O$: Co, 11.94; C, 31.62; H, 6.12; N, 14.18; S, 6.49; Cl, 21.54. Found: Co, 12.2; C, 31.5; H, 6.2; N, 14.1; S, 6.4; Cl, 21.6 Visible spectrum (λ (nm), $\epsilon)_{max}$: 482, 137. ^{1}H NMR: 1.2–1.9 (br), 2.3 (br) (cyclohexane methylenes); 2.6–3.0 (br) (en methylenes); 3.50 (s), 3.59 (s), (N–CH_3, diastereoisomers); 4.2 (m) (CHCl); 4.4 (m) (CH–S–). ^{13}C NMR (mixture of diasteromers): 24.8, 25.0, 25.0, 25.2, 33.3, 33.3, 36.4, 36.7 (cyclohexane methylenes); 42.6, 43.2 (N–CH_3); 44.5, 44.7, 45.5, 45.8, 45.8, 45.8, 46.6, 46.7 (en methylenes); 53.6, 54.6 (CH–S–); 65.8, 66.9 (CHCl); 170.2 (Co—N=C—S); 178.6 (Co—O—C=O).

Base Hydrolysis of $[Co(en)_2(N(CH_3)=C(SC_6H_{10}Cl)CO_2)]Cl_2\cdot0.5H_2O$ (11). The 2-chlorocyclohexyl *N*-methylthiooximidate ester complex **11** (1.0 g) was dissolved in 0.1 M NaOH (20 mL), and the mixture was stirred for 20 min. The reaction mixture was diluted with H_2O (100 mL) and adsorbed on an AG 50W-X2 column (4 × 10 cm). After washing with H_2O (500 mL), the single red band was eluted with 1 M HCl and taken to dryness. ^{1}H and ^{13}C NMR spectra of the residue were identical with those of the *N*-methyloxamato complex **8**. Treatment of a small amount of the 2-hydroxycyclohexyl *N*-methylthiooximidate ester complex **10** dissolved in D_2O in an NMR tube with $NaDCO_3$ also resulted in the formation of the *N*-methyloxamato complex **8**.

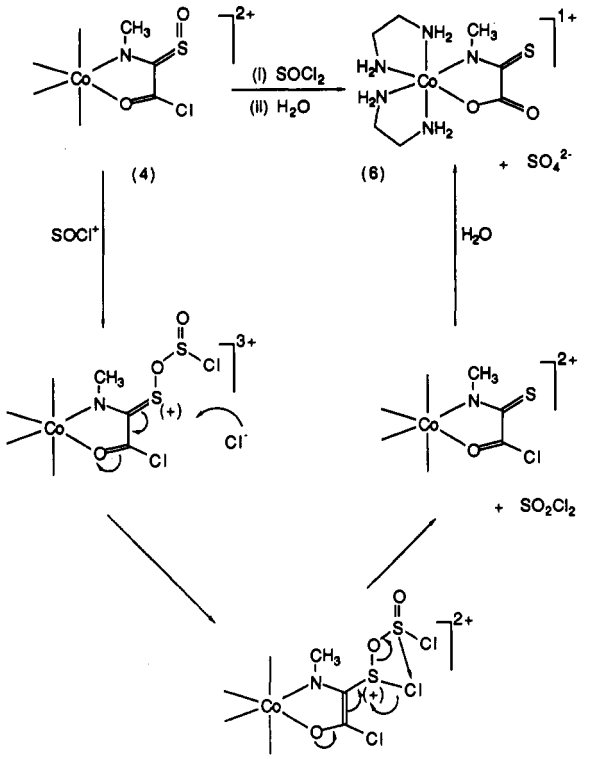
Reaction of $[Co(en)_2(N(CH_3)CSCO_2)]^+$ (6) with Cyclohexene. The trifluoromethanesulfonate salt of the *N*-methylthiooxamate complex **6** (0.112 g) was prepared as before and dissolved in dmf (4 mL). This solution was divided in half and cyclohexene (0.5 ml) added to each part. $SOCl_2$ (0.5 mL) was then added to one of the solutions. On addition of the $SOCl_2$, an orange precipitate was formed, which redissolved within 1 min. After 5 min both solutions were diluted with H_2O (200 mL) and adsorbed on short columns on AG 50W-X2 resin (4 × 4 cm). The columns were washed with H_2O (500 mL) and then eluted with 2 M HCl. Each column gave one band, and these were taken to dryness. The ^{1}H NMR spectrum of the residue from the experiment done without $SOCl_2$ was identical with that of the starting material. The residue from the other experiment (that done with $SOCl_2$) was mostly starting material, but the ^{1}H NMR spectrum also contained some small, broad signals at around 1.3–2.1 ppm, implying that some of the *S*-cyclohexyl complexes **10** and **11** had been formed.

$[Co(en)_2(HN=C(SC_6H_{10}OH)CO_2)]Cl_2\cdot3.5H_2O$ (12) and $[Co(en)_2(HN=C(SC_6H_{10}Cl)CO_2)]Cl_2\cdot2H_2O$ (13). $[Co(en)_2(gly)](CF_3SO_3)_2\cdot CF_3SO_3H$ (**1**) (2 g) was dissolved in dmf (10 mL). Cyclohexene (4 mL) was added followed by $SOCl_2$ (4 mL). The solution rapidly heats up so it was cooled in an ice bath soon after the addition of $SOCl_2$ in order to control this. After 15 min chloroform (30 mL) and then (cautiously) H_2O (100 mL) were added to the solution. The aqueous layer was separated and the chloroform layer extracted twice with H_2O (100 mL). The aqueous layers were combined and diluted with H_2O (800 mL) and adsorbed on a column of AG 50W-X2 resin (4 × 12 cm). Elution with 1 M HCl gave two orange-red bands. The first fraction was taken to near dryness, giving an oil that solidified on trituration with aqueous ethanol. This complex was identified on the basis of its analysis and ^{1}H and ^{13}C NMR spectra as the 2-hydroxycyclohexyl thiooximidate ester complex **12**. Anal. Calcd for $CoC_{12}H_{28}N_5O_3SCl_2\cdot3.5H_2O$: Co, 11.44; C, 27.97; H, 6.85; N, 13.59; S, 6.22; Cl, 13.76. Found: Co, 11.4; C, 28.0; H, 6.5; N, 13.3; S, 6.2; Cl, 14.0. Visible spectrum (λ (nm), $\epsilon)_{max}$: 478, 136. ^{1}H NMR: 1.3–1.9 (br), 2.1 (br) (cyclohexane methylenes); 2.6–3.0 (br) (en methylenes); 3.7 (m) (CHOH); 4.25 (m) (CH–S–). ^{13}C NMR (mixture of diastereoisomers): 24.0, 24.0, 25.3, 25.5, 31.3, 31.4, 35.0, 35.0 (cyclohexane methylenes); 44.4, 44.4, 45.0, 45.0, 45.8, 45.8, 46.3, 46.3 (en methylenes); 51.7, 51.7 (CH–S–); 73.5, 74.5 (CHOH); 171.2 (Co—N=C—S); 180.3, (Co—O—C=O). Fraction 2 was evaporated to near dryness, giving an oil that was taken up in H_2O (10 mL), and red crystals of the 2-chlorocyclohexyl thiooximidate ester complex **13** formed slowly. Anal. Calcd for $CoC_{12}H_{27}N_5O_2SCl_3\cdot2H_2O$: Co, 11.63; C, 28.44; H, 6.17; N, 13.82; S, 6.33; Cl, 20.99. Found: Co, 11.8; C, 29.0; H, 6.3; N, 13.9; S, 6.3; Cl, 21.3. Visible spectrum (λ (nm), $\epsilon)_{max}$: 478, 139. ^{1}H NMR: 1.3–2.0 (br), 2.1 (br) (cyclohexane methylenes); 2.6–3.0 (br) (en methylenes); 4.15 (m) (CHCl); 4.2 (m) (CH–S–). ^{13}C NMR (mixture of diastereoisomers): 24.6, 24.6, 24.6, 24.6, 32.2, 32.4, 36.4, 36.5 (cyclohexane methylenes); 44.2, 44.2, 44.7, 44.7, 45.5, 45.5, 45.9, 45.9 (en methylenes); 51.1, 51.3 (CH–S–); 64.0, 64.1 (CHCl); 170.6 (Co—N=C—S); 179.0 (Co—O—C=O).

Results and Discussion

Reaction of the sarcosinato complex **5** with $SOCl_2$ in dmf gave the *N*-methylthiooxamato complex **6**. It was not immediately clear, however, that this was the product. It could have been the *S*-oxide derivative (**4**, R = CH_3), a sulfine, which arises as a possible product by considering mechanisms for the $SOCl_2$ oxi-

Scheme II



dation of α-amino acidato complexes to α-imino acidato complexes as described in the Introduction. The initial analytical data fitted both possibilities, one with and the other without one water molecule in the lattice, but a subsequent analysis on the anhydrous trifluoromethanesulfonate salt eliminated this possibility. Further, a closely related thiooxamato complex (**15**) has been isolated from reactions of the glycinato complex with $SOCl_2$ and crystallographically characterized.[5]

The first part of the proposed mechanism of formation of the *N*-methylthiooxamato complex **6** is shown as path b in Scheme I (R = CH_3). As is the case for the closely related reactions described previously,[1] the first step is almost certainly the formation of the chelated acid chloride **14** and SO_2Cl^-. This complex would deprotonate readily at the α-methylene group and react with $SOCl_2$ in the same way as the other α-amino acidato complexes to give the chelated α-sulfinyl chloride **3**. Loss of proton H_b and a chloride ion to give the sulfine complex as the acid chloride **4** could then occur. The carbon–sulfur double bond is now in place, but the oxidation level of the sulfur atom is too high. Scheme II illustrates a possible mechanism for this adjustment.

The sulfine complex presumably exists as the acid chloride **4** in the reaction medium. The sulfur–oxygen double bond of sulfines is highly polarized,[6] so that $SOCl_2$ could add across the double bond. This may be a concerted process or, as shown, a stepwise one. Decomposition of this species in the manner illustrated would give SO_2Cl_2 and, on hydrolysis, the *N*-methylthiooxamato complex **6**. On quenching with H_2O, SO_2Cl_2 would hydrolyze to H_2SO_4, which would account for the SO_4^{2-} that is precipitated by the addition of $BaCl_2$. The yield of $BaSO_4$ crudely matches that of the thiooxamato complex **6** (~70% of theoretical yield for both).

A similar type of reaction may be involved when bis(3,4-dichlorophenyl) ether is treated with $SOCl_2$ to yield mainly 2,3,7,8-tetrachlorophenoxathiin and some pentachloro species.[7] The SO_2Cl_2 that is produced in the reaction is responsible for the additional chlorination reactions and, when the reaction is done in the presence of cyclohexene, for the 1,2-dichlorocyclohexane that is also produced.[8]

Longer term reactions of the sarcosinato complex **5** (>15 min) resulted in more complex product distributions. In addition to some decomposition, there were four products from this reaction. The first complex was difficult to obtain in pure form due to the presence of an organic contaminant that was removed by repeated recrystallization from water. It has not been identified as yet, but on the basis of its elemental analysis, an empirical formula has been determined. One possible structure is that of the sulfite ester complex **9**. Its ^{13}C NMR spectrum has multiple peaks in the region of the ethylenediamine methylene signals, indicating that this solid may in fact be a mixture, in spite of the multiple recrystallizations that were performed during its isolation. Some form of isomerism, possibly involving hydrogen bonding to the ethylenediamine ligands, could account for this observation. In any case, the identification of this complex cannot be considered secure.

The second species isolated from these reaction mixtures was the *N*-methylthiooxamato complex **6**, and the third the *N*-methyloxamato complex **8**, and the final, highly charged species appeared to be the dimer complex **7**. The *N*-methyloxamato complex **8** may also be prepared by H_2O_2 oxidation of the *N*-methylthiooxamato complex **6**, by employing long reaction times in the treatment of the sarcosinato complex **5** with $SOCl_2$ or by base hydrolysis of the *N*-methylthiooximidate ester complexes **10** and **11**. It was clearly identified on the basis of its ^1H and ^{13}C NMR spectra and elemental analyses.

The final band in the chromatographic separation of the products from the long-term reactions of $[Co(en)_2(sar)]^{2+}$ with $SOCl_2$ eluted with 4 M HCl. This implied that the species was highly charged. The elemental analyses gave a sulfur to cobalt ratio of 1:2, which along with the high charge implies this complex is a dimer. The possibility of having either Λ or Δ configurations of the ligands around each cobalt follows, which could lead to the presence of diastereoisomers. The splitting observed in the ^{13}C NMR resonances assigned to two of the ethylenediamine methylene carbon atoms is consistent with this analysis. The simplicity of the ^1H and ^{13}C NMR spectra implies a near-symmetrical configuration, and this with the elemental analyses leads to the proposal of **7** as the structure of this complex with ΔΔ, ΛΛ, and ΛΔ configurations of the ligands about the Co ions.

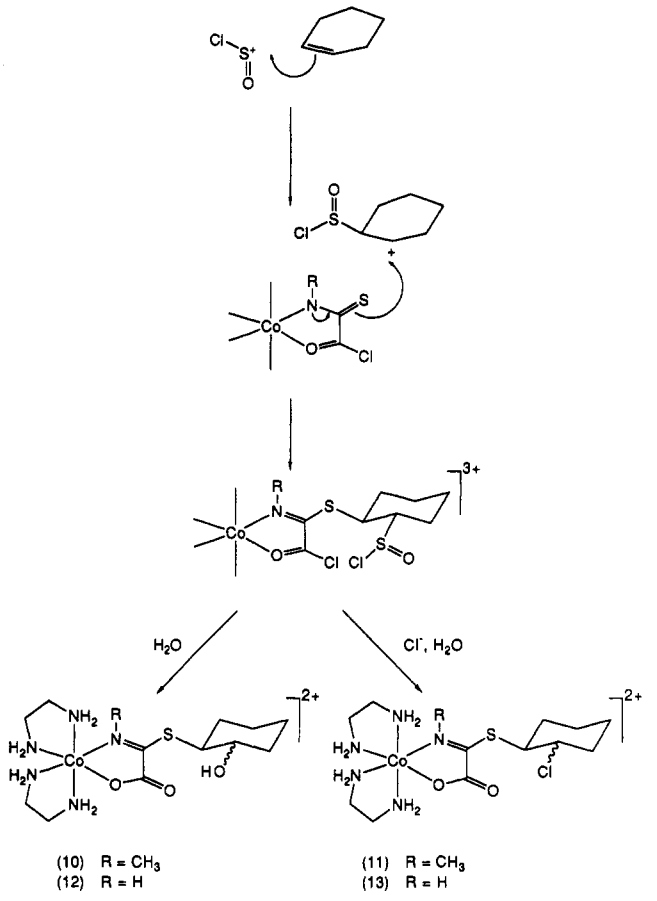
The relative yields of these complexes from the long-term reactions were not so reproducible, but generally speaking, at short reaction times the *N*-methylthiooxamato complex **6** was the major product, while the first and third compounds became more abundant at longer reaction times. The dimer yield, at reaction times greater than about 15 min, was fairly constant at around 15% by weight of the isolated products. The *N*-methylthiooxamato complex **6** was resubmitted to the reaction conditions and gave a product distribution similar to that of the sarcosinato complex. Treatment of the *N*-methylthiooxamato complex **6** with H_2O_2 gave the *N*-methyloxamato complex **8** and elemental sulfur, while treatment with base led only to decomposition.

Given the differences in the starting material, the *N*-methyloxamato complex[1] **8**, which was isolated in small amounts from some of the long-term reactions, is the equivalent product to the *N*-formyloxamato complex. This together with the isolation of small amounts of the thiooxamato complex **15** from reactions of the glycinato complex with fewer equivalents of $SOCl_2$[5] implies that the glycinato and sarcosinato complexes react via very similar pathways. The similar thiooximidate ester products **10–13** obtained from the reactions in the presence of cyclohexene confirms this implication.

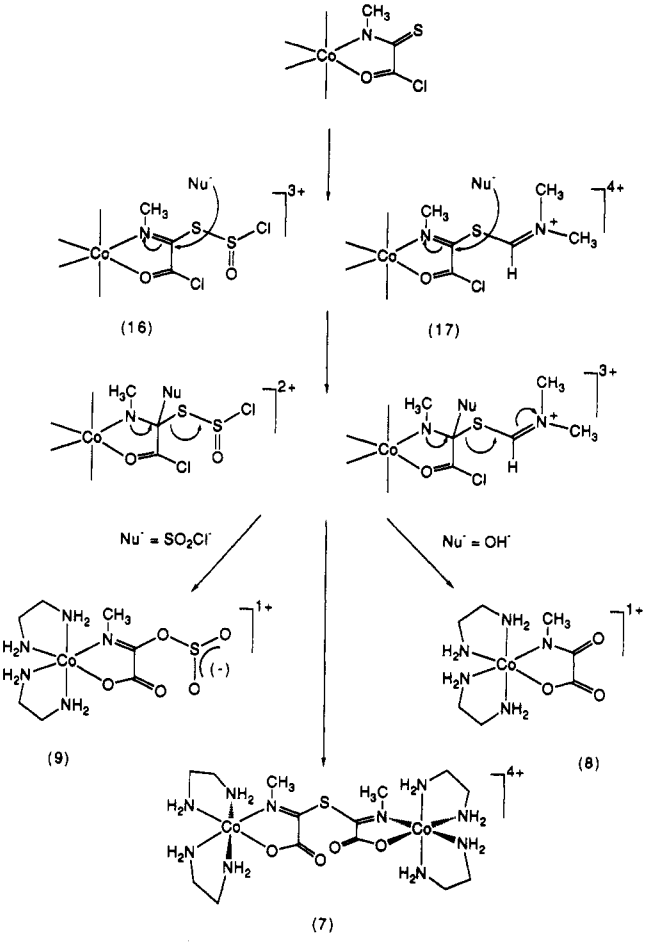
Reaction of the *N*-methylthiooxamato complex **6** with $SOCl_2$ and cyclohexene also gave some *S*-cyclohexyl products, a possible implication being that the thiooxamato complexes, **6** and **15**, are intermediates in these reactions. The presence of the carbon–nitrogen double bond in the structures of these products is readily rationalized by the proposal that the thioxamato complexes, **6** and **15**, or the related acid chlorides have been acting as nucleophiles. However, nucleophilic attack on alkenes is not a common reaction

(5) Grøndahl, L.; Hammershøi, A. Private communication.
(6) Zwanenburg, B.; Thijs, L.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1976**, *86*, 577.
(7) Granoth, I. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2166.
(8) Kharach, M. S.; Brown, H. C. *J. Am. Chem. Soc.* **1939**, *61*, 3432.

Scheme III



Scheme IV



and usually only occurs when there are electron-withdrawing groups on the alkene.[9] It follows that the most likely mechanism for the formation of these complexes is preliminary addition of an electrophile to the alkene, followed by nucleophilic attack by the *N*-methylthiooxamato or thiooxamato complexes on the resulting carbocation as shown in Scheme III.

The near quantitative production of the *S*-cyclohexyl species in these reactions provides an indication of the nucleophilic nature of the *N*-methylthiooxamato and thiooxamato complexes under the reaction conditions. A reasonable speculation is that, in the reaction of the sarcosinato complex **5** with $SOCl_2$, the *N*-methylthiooxamato acid chloride complex exists as an adduct with $SOCl^+$ (**16**) or the Vilsmeier–Haack intermediate (**17**) in the reaction mixture (Scheme IV). Quenching the reaction mixture with H_2O gives the *N*-methylthiooxamato complex **6** plus sulfur dioxide and HCl or dmf. Reaction of the *N*-methylthiooxamate adducts with nucleophiles such as HO^-, SO_2Cl^-, or the *N*-methylthiooxamato complex **6** that may be present in the reaction mixture would, on hydrolysis, give the other observed products from the long-term reactions (the *N*-methyloxamato, sulfite ester, and dimer complexes, respectively), as shown in Scheme IV.

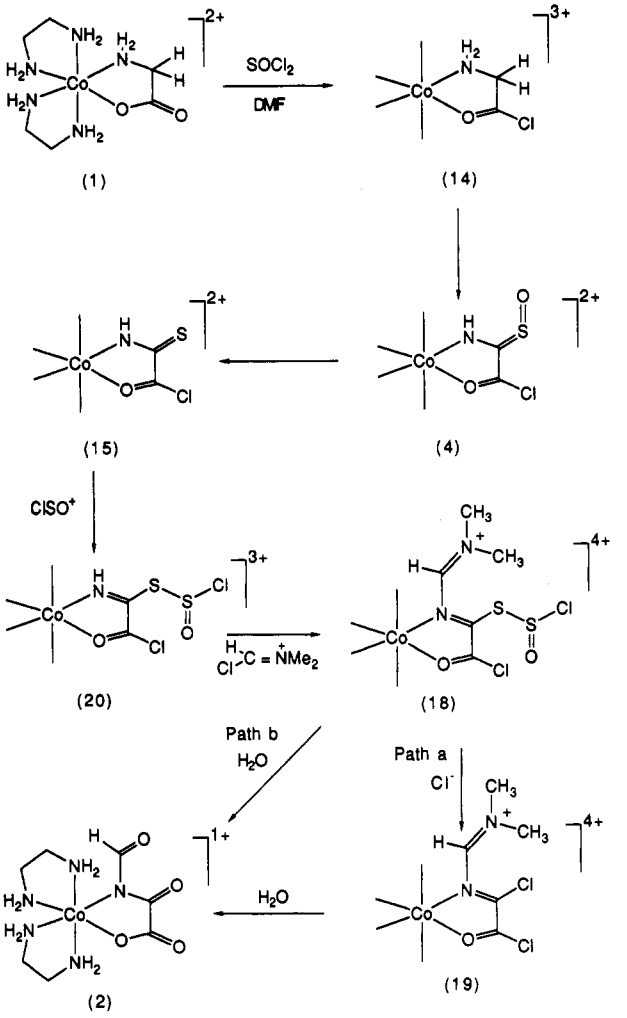
Implications for the $[Co(en)_2(gly)]^{2+}$ Oxidation. In order to draw conclusions about the mechanism of the $[Co(en)_2(gly)]^{2+}$ oxidation on the basis of this work with the sarcosinato complex, it is informative to look at the similarities and differences between the two systems. Clearly, the substrates are very similar, the only difference being the methyl substituent on the amino acid amine group. This would prevent formylation of the amine, one of the events that occurs in conjunction with the glycinato oxidation. Thus, should there be differences in product distributions or reaction rates, then the different N-substituents may be responsible.

One of the products of the long-term reactions of $[Co(en)_2(sar)]^{2+}$ with $SOCl_2$ was the *N*-methyloxamato complex **8**. This is the equivalent of the *N*-formyloxamato complex **2** that results from the oxidation of the glycinato complex **1** in dmf. Apart from the fact that the *N*-methyl group of the sarcosinato complex will prevent an N-formylation reaction, the reaction paths should be the same. The major product from the oxidation of the sarcosinato complex is the *N*-methylthiooxamato complex **6**. Small amounts of the analogous thiooxamato complex **15** have been isolated and characterized crystallographically from $[Co(en)_2(gly)]^{2+}$ oxidations by quenching reactions in which minimal amounts of $SOCl_2$ were employed at low temperatures.[5] These facts imply the same mechanism. Moreover, combining these observations with the fact that the products of the reactions of the sarcosinato and glycinato complexes, **5** and **1**, with $SOCl_2$ in the presence of excess cyclohexene are almost identical allows a high degree of similarity between their reaction paths to be inferred.

A possible mechanism for the oxidation of the glycinato complex **1** is shown, in broad terms, in Scheme V. In this proposal, the glycinato complex **1** is converted into the chelated acid chloride, which then reacts with $SOCl_2$, in an manner identical with that shown in path b of Scheme I, to give the sulfine complex **4**. Deoxygenation by $SOCl_2$ via the mechanism shown in Scheme II will give the thiooxamato complex **15**, which can then react with the most common electrophile, probably $SOCl^+$, to give the adduct **20**. If cyclohexene is present, then the most common electrophile may well be the intermediate shown in Scheme III, yielding the *S*-cyclohexyl complexes, **12** and **13**. If cyclohexene is not present, it is at this point that the reactions of the glycinato and sarcosinato complexes, **1** and **5**, deviate somewhat. The glycinato reaction continues rapidly on to the *N*-formyloxamato complex **2**, while the sarcosinato reaction products remain substantially unchanged at this stage, with only slow reaction to give the *N*-methyloxamato complex **8** and other products. The implication is that the difference between the complexes must therefore affect the next step. Accordingly, the next step in the proposed mechanism for the transformation of the glycinato

(9) Whitham, G. H. In *Comprehensive Organic Chemistry*; Barton, D.; Ollis, W. D., Eds.; Pergamon Press: London, 1979; Vol. 1, p 154.

Scheme V



complex is deprotonation at the imine nitrogen atom and reaction with the Vilsmeier–Haack intermediate to give the dimethyliminium species **18**. The presence of this substituent will facilitate the attack by a nucleophile, a chloride or SO_2Cl^- ion, via path a to give the *N*-dimethyliminium oxalyl chloride derivative **19** or the related sulfite ester. Quenching with H_2O should hydrolyze the two acid chlorides and the dimethyliminium group to afford the observed *N*-formyloxamate product **2**. An alternative could involve direct reaction of **18** with H_2O as shown in path b. In this proposal, the presence of the dimethyliminium group is presumed to favor attack of the H_2O on the imine carbon atom rather than on the sulfinyl chloride, since the *N*-formyloxamato complex **2** is the observed product rather than the *N*-formyl derivative of the thiooxamato complex **15**.

The products of the reaction of these complexes with $SOCl_2$ and cyclohexene provide some evidence for the formylation occurring at this point in the reaction sequence. It should be noted that the *S*-cyclohexyl complexes derived from the glycinato complex could conceivably undergo a similar formylation reaction. Nucleophilic attack on this species should also then give rise to the *N*-formyloxamato complex **2**. Why does it not do this?

The ^{13}C NMR spectra of the products of the reaction of the sarcosinato complex with $SOCl_2$ and cyclohexene reveal the presence of diastereoisomers. The largest chemical shift differences between the equivalent signals of the two sets of diastereoisomers were for signals assigned to the methine carbon atoms of the cyclohexane ring. This is not unexpected, as these centers are associated with the observed diastereoisomers. However, the *N*-methyl group resonance also showed a large difference in chemical shift between the diastereoisomers. This can be interpreted on the basis that the cyclohexane ring lies relatively close to the methyl substituent. If it is assumed that the cyclohexane ring is similarly disposed in the products derived from the glycinato complex, then there would be considerable steric hindrance to the approach of the Vilsmeier–Haack intermediate and consequently no formylation. Without the activating effect of the dimethylminium substituent the hydrolysis reaction is very slow, as it is for the *N*-methylthiooxamate–$SOCl^+$ derivative **16**, and none of the *N*-formyloxamato complex **2** is formed from the *S*-cyclohexyl compounds, **12** and **13**, in the reaction time.

Conclusion

The reactions are triggered by the increase in acidity of the protons on the α-carbon atom of the chelated amino acid chloride. The proton exchange at these sites appears to be rather rapid, even under the mild conditions of the reactions described here, but it is not likely to be completely deprotonated. Even so, the small concentration of carbanion produced is efficiently captured by the electrophiles in solution.

The results of the reaction of the sarcosinato complex **5** with $SOCl_2$ described in this paper provide evidence in support of a mechanism for the formation of the *N*-formyloxamato complex **2** from the glycinato complex **1** under the same conditions. The results imply that the reaction proceeds via the sulfine complex **4** to the thiooxamato complex **15**. This last complex is highly reactive toward electrophiles, a property demonstrated by the formation of a series of new thiooximidate ester complexes **10–13** when it is generated in the presence of cyclohexene. Further reaction leads, after hydrolysis, to the oxamato complexes **2** and **8**. The vastly different rates for the reaction of the thiooxamato and *N*-methylthiooxamato complexes, **15** and **6**, implies that formylation of the imine nitrogen atom in species such as the thiooxamato–$SOCl^+$ adduct **20** activates the molecule toward hydrolysis. The rapid reaction of the glycinato complex **1** to give the *N*-formyloxamato complex **2**, rather than the thiooxamato complex **15**, may be attributed to the vulnerability of the thiooxamate–$SOCl^+$ adduct **20** toward formylation.

Acknowledgment. Support from the Danish Natural Science Research Council is gratefully acknowledged and we thank the ANU Microanalytical Unit for analyses.