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Transition Metal Complexes of the Zwitterionic Amino Acid DL-Methylsulfoniummethioninate and of the Amido Acid Derived from it by Facile Amine Deprotonation

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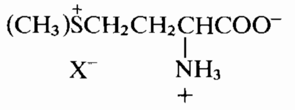
The reaction of the zwitterionic dl-methylsulfoniummethioninate, $(CH_3)_2SCH_2CH_2CH(NH_2)COO^-$, with chromium(III), cobalt(II), nickel(II), copper(II), and zinc(II) salts have been examined. These mostly give rise to formation of octahedral complexes containing either bidentate or tridentate aminocarboxylate coordination. Under facile conditions the metal ions catalyse the deprotonation of the amino nitrogen to yield complexes of the amido acid $(CH_3)^+SCH_2CH_2CH(NH)COO^-$. The unusual reactions of these ligands and the unusual properties of some of the resulting complexes is thought to be due, at least in part, to the formal anionic and cationic centers which exist in these species. The complexes were characterized by magnetic measurements and by visible reflectance and infrared spectral measurements.

Introduction

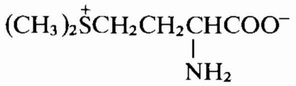
Coordination chemists have been interested for many years in the donor properties of amino acids as models for metal–protein interaction. We have paid particular attention to sulfur-containing amino acids and have engaged upon studies of divalent and trivalent metal ions complexed to methionine[1], S-methylcysteine[2], penicillamine[3], glutathione[4], and cysteine[5]. The *in vivo* interaction of such amino acids incorporated into peptides is of immense biological importance[6], *e.g.* as in methionine biosynthesis from methylcobalamin and homocysteine.[7,8] Similarly the treatment of the disorder of copper metabolism known as Wilson's disease with 1-penicillamine adds another dimension to the interest in this type of chemistry.[9] This area has also received attention because of the development of the Hard–Soft Acid–Base theory; sulphur-containing amino acids possess both class *b* (thioether or sulfide) and class *a* (amino and carboxylato) donors.

Because of the biological significance of the interaction of methyl groups with sulfur centers[7,8] we have embarked upon a study of the reaction of the cationic species methylsulfoniummethionine, and a preliminary note of some aspects of this work has already been published.[10] In the salts of *dl*-methylsulfoniummethionine (LHCl)(I) the amino acid moiety exists, as do all amino acids, as a zwitterion in the solid state. However, even after deprotonation of the ammonium group upon complexation the resulting ligand (II) will still be zwitterionic and coordinate as a formally neutral ligand, L. We were further stimulated in beginning this investigation by the prospect of the interesting reactions of metal ions with a ligand with opposite charges on its peripheries. Cationic ligands have recently been shown to have unusual coordination properties.[11]



$$\underset{X^-}{(CH_3)\overset{+}{S}}CH_2CH_2\underset{\underset{+}{NH_3}}{\underset{|}{C}}HCOO^-$$

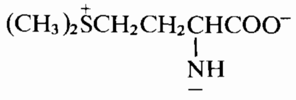
LHX (I)



$$(CH_3)_2\overset{+}{S}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOO^-$$

L (II)

Our expectations were fulfilled for, as well as isolating fifteen complexes of the neutral, zwitterionic ligand, L, we have discovered that catalytic deprotonation of the amino group of L occurs under certain conditions upon reaction with cobalt(II), nickel(II), copper(II), and zinc(II) salts to form complexes containing the anionic ligand, L′, (III). Seven complexes of this highly unusual ligand are reported here.



$$(CH_3)_2\overset{+}{S}CH_2CH_2\underset{\underset{-}{NH}}{\underset{|}{C}}HCOO^-$$

L′ (III)

Experimental

Starting Materials

DL-methylsulfoniummethionine chloride (Nutritional Biochemicals Corporation) and analytical grade metal salts were used without further purification.

Preparation of the Other Ligand Derivatives

DL-methylsulfoniummethionine perchlorate, $LHClO_4$

The chloride, LHCl, (8.0 g; 0.04 mol) was suspended in methanol (100 ml) and sufficient water was added until the suspension just dissolved. Lithium perchlorate (14 g; 0.132 mol), dissolved in the minimum quantity of water, was added to this solution with stirring, and after 3–4 minutes fine white crystals separated. The crystals were filtered, washed with ethanol (50 ml) and dried *in vacuo* over P_4O_{10}. Yield 92%. Analysis: Found C, 27.6; H, 5.5; N, 5.3%. Calculated for $C_6H_{14}O_6SNCl$ C, 27.4; H, 5.3; N, 5.3%.

DL-methylsulfoniummethionine bromide, LHBr

A 2N solution of sodium bromide in water was run through a Dowex 1–X8 anion exchange resin column, and then the column was washed thoroughly with triply distilled water. The LHCl (4 g) was dissolved in water (80 ml) and passed through the column. The resulting solution was evaporated to dryness over a steam bath and then further dried *in vacuo* over P_4O_{10}. Analysis: Found C, 29.8; H, 5.9; N, 5.8; Br, 32.6%. Calculated for $C_6H_{14}O_2SNBr$ C, 29.5; H, 5.7; N, 5.5; Br, 32.8%.

DL-methylsulfoniummethionine iodide, LHI

This was prepared in an analogous manner to the LHBr derivative. Analysis: Found C, 24.8; H, 4.8; N, 4.8; I, 43.4%. Calculated for $C_6H_{14}O_2$ SNI C, 24.7; H, 4.8; N, 4.6; I, 43.3%.

Preparation of the Complexes

Bis-(DL-methylsulfoniummethioninato)aquocopper(II) perchlorate, $[CuL_2(H_2O)](ClO_4)_2$

To DL-methylsulfoniummethionine perchlorate (1.5 g; .0057 mol) in water (50 ml) was added copper(II) carbonate (0.3 g; .0024 mol). The mixture was heated at 60 °C with stirring for 1 hr, after which the blue solution was filtered while hot and then allowed to stand in a refrigerator for 12 hr. The blue needles were filtered, washed with 95% ethanol (50 ml) and then dried *in vacuo* over P_4O_{10}.

The other *perchlorate* complexes: $[CrL_3](ClO_4)_3$, $[CoL_3](ClO_4)_2$, $[NiL_2](ClO_4)_2$, and $[ZnL_2](ClO_4)_2$ were prepared in an analogous manner. For the chromium(III) complex freshly precipitated chromium(III) carbonate was made from $Cr(H_2O)_6Cl_3$ and $NaHCO_3$, and washed thoroughly with water before use.

Dichlorobis-(DL-methylsulfoniummethioninato)copper(II), $[CuL_2Cl_2]$

DL-methylsulfoniummethionine chloride (1.0 g; 0.005 mol) was mixed with lithium hydroxide monohydrate (0.22 g; 0.0055 mol) in ethanol (50 ml) at 65 °C. After stirring for 15 min the hot solution was filtered to remove excess LiOH.

The filtrate was cooled and then slowly added to anhydrous cupric chloride (0.68 g; 0.005 mol) in ethanol (20 ml) leading to the immediate formation of a dark green precipitate. This was filtered, washed with 95% ethanol (50 ml) and dried *in vacuo* over P_4O_{10}. The chromium(III) complex $[CrL_3]Cl_3$, was made by analogous means.

Dichloro-DL-methylsulfoniummethionatonickel(II), $[NiLCl_2]$

To a refluxing suspension of DL-methylsulfoniummethionine chloride (1.0 g; 0.005 mol) in ethanol (60 ml) was added a solution of anhydrous nickel(II) chloride (0.65 g; 0.005 mol) in ethanol (40 ml). After refluxing for 2 hr, the dark green solid which had resulted was filtered, washed with hot 95% ethanol (40 ml), and dried *in vacuo* over P_4O_{10}.

Dichloro-DL-methylsulfoniummethioninatocobalt(II), $[CoLCl_2]$

The ligand chloride (1.0 g; 0.005 mol) was suspended in ethanol (70 ml) and refluxed for 2 hr with anhydrous cobalt(II) chloride (0.434 g; 0.003 mol). The bright blue product which formed was filtered in a dry box and washed with ethanol (40 ml). After drying elemental analysis showed this product to have the formula $Co_2(LCl)_3Cl_4$. This bright blue solid (1.0 g; 0.00117 mol) was mixed with $LiOH\cdot H_2o$ (0.147 g; 0.0036 mol) in ethanol (80 ml) and stirred at 65 °C. After stirring for 5 min the solid became blue-green in color, and after a further 10 min stirring the resulting compound was filtered, washed with ethanol (30 ml), and dried *in vacuo* over P_4O_{10}.

Trichlorobis(DL-methylsulfoniummethioninato)chromium(III), CrL_2Cl_3

Hydrated chromium(III) chloride (0.40 g; 0.0015 mol) was heated in an oven at 100 °C for 20 hr and then dissolved in ethanol (60 ml). This solution was slowly added to a refluxing suspension of the ligand chloride (1.0 g; 0.005 mol) in ethanol (80 ml), and refluxing was continued for 2 hr. The gray compound which eventually precipitated was filtered from the hot solution, washed with hot ethanol (100 ml), and dried *in vacuo* over P_4O_{10}.

The bromo complexes, $[CuL_2Br_2]$, $[CoL_3][CoBr_4]$, $[ZnLBr_2]$, and $[CrL_3]Br_3$, and the iodo complex, $[CrL_3]I_3$, were made by methods analoguous to those used to prepare the perchlorate complexes.

Complexes Containing the Methylsulfoniummethioninate Anionic Ligand, L'

A solution of the lithium salt of DL-methylsulfoniummethionine chloride was prepared in ethanol as described above:

[NiL'Cl] was obtained as a green precipitate when the Li(L)Cl solution was added to nickel(II) chloride in ethanol (molar ratio 1 : 1).

When the order of addition was reversed and an ethanolic solution of nickel(II) chloride was added to the Li(L)Cl solution (molar ratio 1 : 2) $[NiL'_2]$ and (molar ratio 1 : 3) $Li[NiL'_3]$ were obtained.

A light green precipitate of [CuL'Cl] was immediately formed when cupric chloride in ethanol was added to an equimolar solution of Li(L)Cl in ethanol.

Adding an equimolar ethanolic solution of zinc(II) chloride to Li(L)Cl resulted in eventual precipitation of [ZnL'Cl], but when the $ZnCl_2$: Li(L)Cl ratio was 1 : 3 this reaction yielded $[ZnL'_2]$.

Physical Measurements

Metal analyses were carried out by titration with E.D.T.A.[12], and other analyses were performed by the microanalytical laboratory of UMIST. Infrared absorption spectra in KBr disks and Nujol mulls were obtained on a Perkin–Elmer model 221 recording spectrophotometer, and diffuse reflectance spectra were obtained using a Beckman DU quartz spectrophotometer using $MgCO_3$ as the reference. Magnetic susceptibility measurements were performed by the Gouy method.

Deuterated Compounds

The ligand hydrochloride and the lithium salt derivative were deuterated by crystallization from 95% deuterium oxide. Deuteration of the complexes were obtained by standing the complexes in dessicators under a partial pressure of D_2O for 12 hr.

Results and Discussion

We have found that reaction of the perchlorate or halide salts of methylsulfoniummethionine in ethanol or water with transition metal salts results in the elimination of HX (X = ClO_4, Cl, Br, I) and the

TABLE I. Physical Properties and Analytical Data of the Complexes.

Complex	Color	M.Pt. or Decomp. Pt.	μ_{eff}, B.M.	Metal		Nitrogen		Halide	
				% Calc.	% Fd.	% Calc.	% Fd.	% Calc.	% Fd.
L = $\{(CH_3)_2SCH_2CH_2CH(NH_2)COO\}$									
$[CrL_3](ClO_4)_3$[a]	light pink	200°C	3.76	5.00	4.89	6.21	6.31		
$[CrL_3]Cl_3$	light pink	>300	3.70	8.03	7.81	6.49	6.60	16.45	16.68
$[CrL_3]Br_3$[b]	light pink	145	3.68	6.66	6.35	5.38	5.51	30.70	31.00
$[CrL_3]I_3$	light pink	167	3.70	5.64	5.30	4.56	4.61	41.32	41.28
CrL_2Cl_3[c]	gray	140	3.79	10.73	10.51	5.78	5.83	21.98	21.80
$[CoL_3](ClO_4)_2$[d]	pink	195	4.89	7.83	7.80	5.60	5.60		
$[CoLCl_2]$	blue–green	205	4.34	20.17	19.99	4.18	4.13	24.21	24.28
$[CoL_3][CoBr_4]$	light purple	90	4.79[e]	12.73	12.90	4.53	4.51	34.50	35.20
$[NiL_2](ClO_4)_2$[f]	blue–green	195	3.12	10.06	10.20	4.80	5.00		
$[NiLCl_2]$[g]	light green	>300	3.38	20.05	18.85	4.78	4.61	24.26	24.37
$[CuL_2Cl_2]$	dark green	133	2.16	13.80	13.60	6.08	6.19	15.40	15.60
$[ZnL_2](ClO_4)_2$[h]	white	150		11.00	11.19	4.70	4.60		
$[ZnLBr_2]$[i]	white	164		16.84	17.00	3.61	3.67	41.17	41.17
L' = $\{(CH_3)_2SCH_2CH_2CH(NH)COO\}^-$									
$Li[NiL'_3]$[j]	light blue	>300	3.24	10.58	10.62	7.57	7.66		
$[NiL'_2]$[k]	light blue	>300	3.28	15.26	15.10	7.28	7.15		
[NiL'Cl][l]	light green	>300	3.38	22.82	22.62	5.44	5.45	13.80	13.64
$Li[CoL'_3]$	pink	200	5.14	10.62	10.68	7.57	7.53		
[CuL'Cl][e]	light green	150	1.77	24.24	24.39	5.34	5.31	13.93	13.75
[ZnL'Cl]	white	165		24.78	24.61	5.31	5.37	13.45	13.39
$[ZnL'_2]$[m]	white	290		16.71	16.95	7.19	7.33		

[a] Calc. C, 25.7, H, 4.7%. Fd. C, 25.9; H, 4.8%. [b] Calc. C,27.7; H, 5.0%. Fd. C, 27.9; H, 5.3%. [c] Calc. C, 29.8; H, 5.4%. Fd. C, 29.6; H, 5.5%. [d] Calc. C, 28.9; H, 5.1%. Fd. C, 29.2; H, 4.8%. [e] Moment of the cation after subtracting 9.144 × 10^6 cgs from total $\chi_{M(Corr.)}$ to allow for anion. [f] Calc. C, 24.7; H, 4.4%. Fd. C, 24.9; H, 4.4%. [g] Calc. C, 23.7; H, 4.7% Fd. C, 23.6; H, 4.9%. [h] Calc. C, 23.7; H, 4.7%. Fd. C, 23.4; H, 4.3%. [i] Calc. C, 18.6; H, 3.4%. Fd. C, 18.8; H, 3.6%. [j] Calc. C, 39.1; H, 6.5%. Fd. C, 38.9; H, 6.4%. [k] Calc. C, 37.8; H, 6.3%. Fd. C, 37.9; H, 6.5%. [l] Calc. C, 27.5; H, 4.6%. Fd. C, 27.7; H, 4.7%. [m] Calc. C, 37.1; H, 6.2%. Fd. C, 36,7; H, 6,0%.

formation of metal complexes of the neutral zwitterionic ligand L, (II) (Table I). The reaction of $LiOH \cdot H_2O$ with LHCl in ethanol produces a solution which reacts with metal salts to produce, under some conditions, complexes of neutral L, yet under fairly similar conditions reacts with nickel(II), cobalt(II), copper(II), and zinc(II) chlorides to produce complexes of the anionic ligand L′ (III).

Complexes of the Neutral Ligand, L

Of the five chromium(III) complexes isolated four have similar donor sets, $[CrL_3]X_3$ ($X = ClO_4$, Cl, Br, I). Ligand field theory predicts that octahedral chromium(III) complexes should have magnetic moments close to, but slightly below, the spin-only value of 3.88 B.M., and we find that the pink complexes here have values in the range 3.68–3.76 B.M., in good agreement with theory. Of the three spin-allowed electronic transitions[13] we have observed the $^4T_1(F) \leftarrow {}^4A_2$ and $^4T_2 \leftarrow {}^4A_2$ transitions at *ca.* 26.3 kK and *ca.* 19.0 kK, respectively (Table II). The third transition, $^4T_1(P) \leftarrow {}^4A_2$, occurs in the ultraviolet in the range 40–35 kK and we did not scan this range of the spectrum. The almost identical electronic band positions is good evidence for similar coordination chromophores, $[CrL_3]^{3+}$, and for non-coordination of the anions. Moreover, the infrared spectrum of $[CrL_3](ClO_4)_3$ both in Nujol and KBr disk exhibits only unsplit bands at 1098 cm^{-1} and 620 cm^{-1}, indicative of ionic perchlorate groups.[14]

The free zwitterion, isolated from the reaction of $LiOH \cdot H_2O$ with LHCl exhibits ν(NH) frequencies at 3372 and 3296 cm^{-1} (Table III). In the $[CrL_3]^{3+}$ complexes the same vibrations absorb at considerably lower frequencies, *ca.* 3220–3110 cm^{-1}, which is indicative of strong chromium–amine bonds.[1, 15] Similarly, the $\nu(COO^-)$ frequencies of a monodentate

TABLE III. Solid State Electronic Spectral Maxima (kK).

$[CrL_3](ClO_4)_3$	26.3, 19.2
$[CrL_3]Cl_3$	25.1, 18.7
$[CrL_3]Br_3$	26.3, 19.2
$[CrL_3]I_3$	26.3, 19.4
CrL_2Cl_3	23.1, 17.4
$[CoL_3](ClO_4)_3$	18.73
$[CoLCl_2]$	4.95, 5.88, 7.01, 14.81, 15.77, 16.26
$[CoL_3][CoBr_4]$	4.36, 4.91, 5.79, 13.78, 14.00, 14.97 15.40, 18.98
$[NiL_2](ClO_4)_2$	9.3, 12.3, 15.63, 26.3
$[NiLCl_2]$	8.7, 11.0, 15.2, 23.8
$[CuL_2Cl_2]$	13.9
$Li[NiL'_3]$	9.71, 14.81, 16.33, 27.4
$[NiL'_2]$	9.09, 15.15, 25.64
$[NiL'Cl]$	8.2, 14.2, 24.6
$Li[CoL'_3]$	18.90
$[CuL'Cl]$	13.1

TABLE II. Some Significant Infrared Absorption Frequencies of the Complexes.[a]

	$\nu(NH_2)$ or $\nu(NH)$	$\nu(COO^-)$ asym	$\delta(NH_2)$ or $\delta(NH)$	$\nu(COO^-)$ sym	$\Delta\nu(COO^-)$
LHCl	3500–3100 v. br	16245	1595s	1403m	221
Li(LHCL)	3372m, 3296m	1608sh	1576s	1448m	160
$[CrL_3](ClO_4)_3$	3191m, 3036s	1639s	1601m	1403m	236
$[CrL_3]Cl_3$	3220s, br, 3110s, br	1639s	1595m	1398s	241
$[CrL_3]Br_3$	3220–3105s, br	1635s	1600m	1400s	235
$[CrL_3]I_3$	3220–3110s, br	1635s	1595m	1402s	233
CrL_2Cl_3	3200–3000br	1630s	1620sh	1404s	226
$[CoL_3](ClO_4)_2$	3333s, 3250s, 3170m	1634s	1608sh	1425s	209
$[CoLCl_2]$	3148s, br, 3020s, 3014sh	1612s	1580m	1425s	187
$[CoL_3][CoBr_4]$	3250s, 3170m	1635s	1608sh	1425s	210
$[NiL_2](ClO_4)_2$	3335s, 3282m, 3241sh	1630s	1570sh	1420s	210
$[NiLCl_2]$	3300s, br, 3012m	1630s		1416s	214
$[CuL_2Cl_2]$	3232s, 3130sh, 3040m	1622s	1579sh	1394s	228
$[ZnL_2](ClO_4)_2$	3325s, 3272s, 3166sh	1620		1426s	194
$[ZnLBr_2]$	3295s, br, 3250sh, 3150sh	1602s	1571sh	1425m	177
$Li[NiL'_3]$	3328m, 3230m, br, 3169sh	1617sh	1588s	1406m	211
$[NiL'_2]$	3245m, br, 3145w	1620sh	1592s	1415m	205
$[NiL'Cl]$	3400–3250s, br	1600s, br	1600	1407m	193
$Li[CoL'_3]$	3400–3200m, br	1610s	1590s, br	1389m	221
$[CuL'Cl]$	3280–3230m, br, 3130sh	1630s	1592s	1432m	198
$[ZnL'Cl]$	3302m 3256m	1601s	1569sh	1428m	173
$[ZnL'_2]$	3305m, 3256m	1604s	1569sh	1428m	176

[a] s = strong, m = medium, w = weak, br = broad, sh = shoulder.

carboxylate group shift from their positions in the ionic, non-bonded symmetrical COO$^-$ group, because of the asymmetry introduced into this group by monodentate coordination.[1,16] The difference in Δ, the separation between the ν(COO$^-$ asym) and ν(COO$^-$ sym), between the zwitterionic ligand, L, and the metal complexes $[CrL_3]^{3+}$ suggests a strong Cr–O covalent bond, as might be expected for a trivalent metal ion.

The grey CrL_2Cl_3 complex decomposes in water and is insoluble in organic solvents, and thus conductivity measurements were not obtainable. Nonetheless a formulation as $[CrL_2Cl_2]Cl$ seems justifiable. The electronic spectrum of this complex in the solid state (Table II) indicates an octahedral stereochemistry (in fact, almost all chromium(III) complexes are octahedral[17]), and the lowest energy absorption, which according to ligand field theory is equal to lODq, is at a lower energy than in the spectra of the $[CrL_3]^{3+}$ complexes, which is what may be expected to result upon replacement of an aminocarboxylato group by two chloride ligands in the $[CrL_3]^{3+}$ moeity.

The pink $[CoL_3](ClO_4)_2$ has a magnetic moment, 4.89 B.M., typical of octahedral cobalt(II) complexes, and the visible spectrum exhibits only one absorption at 18.73 kK. That the $[CoL_3][CoBr_4]$ compound also contains this cation is evidenced by the same absorption, assigned to the transition $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, at 18.98 kK (Table II).

The magnetic moment, 3.12 B.M., of $[NiL_2](ClO_4)_2$ is typical of octahedral nickel(II) complexes, and since the infrared spectrum shows the perchlorate groups to be ionic, it is apparent that the ligands are acting as tridentate donors. The electronic spectrum of $[NiL_2](ClO_4)_2$ is remarkably similar to that of $[NiMt_2]$ (Mt = anion of *dl*-methionine)[1] which contains a $[NiN_2O_{4\,(bridging)}]$ coordination environment. Such an environment has been shown to exist by X-ray studies in the $[CuMt_2]$ complex,[18] each ligand chelating via O and N donors with a bridging O donor as well; the carboxylate bridge is unsymmetrical. Similarly, the electronic spectral evidence indicates that the $[NiLCl_2]$ complex is hexacoordinate, but the magnetic moment of 3.38 B.M. suggests that there is considerable distortion from octahedral symmetry.[19] This complex, too, must be polymeric and may contain both bridging carboxylato and chloro ligands.

The dark-green complex CuL_2Cl_2 differs considerably from the blue–purple [Cu(aminoacidato)$_2$] complexes and this color difference is no doubt due to the coordination of chloride ligands. We have formulated this complex as the hexacoordinate $[CuL_2Cl_2]$. The possibility that it was a pentacoordinate $[CuL_2Cl]Cl$ species was seemingly excluded when a suspension of the complex in ethanol was stirred with a solution of sodium tetraphenylborate: after 30 minutes both reactants were recovered unchanged.

The infrared spectra of $[ZnL_2](ClO_4)_2$ and $[ZnLBr_2]$ are remarkably similar to the nickel(II) complexes, $[NiL_2](ClO_4)_2$ and $[NiLCl_2]$, and may thus be assigned similar hexacoordinate structures.

Complexes of the Amido Acid, L'

Reaction of the zwitterion, L, in ethanolic solution with nickel(II) salts leads to the isolation of three complexes, Li[NiL'$_3$], [NiL'$_2$], and [NiL'Cl]. In these complexes the original neutral methylsulfoniummethioninate zwitterion has become an anion. The zwitterion (II) may become an anion by either loss of an S-bonded methyl group and becoming the methioninate species or by deprotonation of the amino group forming an amido acid. All the evidence suggests that the latter has occurred and these reactions are at once surprising and mystifying. The metal-ion catalysed deprotonation of L occurs when Li(L)Cl is added to $NiCl_2$ in ethanol to form [NiL'Cl], but the exactly analogous reaction between Li(L)Cl and $CuCl_2$ produces $[CuL_2Cl_2]$. In order to produce [CuL'Cl] the order of addition must be reversed.

Deprotonation of coordinated amino groups has been achieved by Watt and co-workers[20–22] in a number of cases, but only under fairly drastic conditions. Thus, in contrast to the facile deprotonations reported here, Watt *et al.* converted bis(glycinato) nickel(II), $[Ni(NH_2CH_2COO)_2]$ into the mono- and di-deprotonated species, $K[Ni(NHCH_2COO)(NH_2CH_2COO)]$ and $K_2[Ni(NHCH_2COO)_2]$ respectively, by reaction with KNH_2 in liquid ammonia at –33.5 °C. As we have never experienced any tendency for complexes of the simple amino acid DL-methionine to deprotonate we can only conclude that the ready tendency of the amino group to deprotonate in methylsulfoniummethioninate is due to the presence of a positive charge located four atoms away from the nitrogen.

All the nickel(II) complexes of the amido acid (Table I) are octahedral, as evidenced by their electronic spectra (Table II). The baricenter rule[23] is extremely useful in assigning chromophore types in nickel(II)–N,O donor systems. The Li[NiL'$_3$] spectrum is a fairly typical $[NiN_3O_3]$ example,[24] whilst the slightly lower ligand field strength exhibited by the bridging carboxylato group is reflected in the spectrum of the $[NiN_2O_{4\,(bridging)}]$ moeity. The light-green [NiL'Cl] complex must be highly polymeric with a number of bridging ligands if its hexacoordinate spectrum is to be accounted for. It has a magnetic moment of 3.38 B.M.

The Li[CoL'$_3$] complex exhibits a reflectance spectrum very similar to that of $[CoL_3](ClO_4)_2$, but its magnetic moment, 5.14 B.M., indicates considerable contribution from spin-orbit coupling.

By analogy with [NiL'$_2$] the [ZnL'$_2$] species is also assigned a hexacoordinate structure, as the infrared spectra of these complexes have almost identical spectra. In contrast the spectral profiles of [CuL′Cl] and [ZnL′Cl] differ significantly from that of [NiL′Cl], and so the two former complexes may well be four-coordinate.

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