Selenourea as a Ligand: Visible and Infrared Spectra of Some Complexes of Selenourea with Cobalt, Zinc, Cadmium, and Mercury

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The donor properties of selenourea (su) are in general very similar to those of thiourea. Ligand field parameters derived from the visible spectra of $Co(su)_4(ClO_4)_2$ and $Co(su)_4(NO_3)_2$ are $10\,Dq$ = 4040 cm^{-1}, β = 0·61. The i.r. spectrum of co-ordinated selenourea is discussed in terms of the calculated potential energy distribution for the planar vibrations of selenourea. Metal–selenium stretching vibrations lie in the frequency range 245—167 cm^{-1} decreasing in the order M = Co > Zn > Cd > Hg. The ratio νMSe : νMS in comparable selenourea and thiourea complexes is approximately 0·80. The mercury(II) complex $Hg(su)_2Br_2$ probably contains planar $[Hg(su)_2Br]^+$ ions, but the structures of $Hg(su)_2Cl_2$ and $Hg(su)_2I_2$ cannot be determined with any degree of certainty from the i.r. data alone.

We have recently described[1,2] normal co-ordinate calculations for the planar vibrations of urea and thiourea, and have made frequency assignments for selenourea. Although complexes containing urea[3,4] or thiourea[4-11] as ligands have been thoroughly studied there is relatively little information available concerning the donor properties of selenourea,[10-12] no doubt because it is considerably less stable than the other two compounds. We have now prepared a representative series of cobalt, zinc, cadmium, and mercury complexes of selenourea for comparison with their already well characterised thiourea analogues.

Table 1

Selenourea complexes

	Found %			Calc. %		
	N	X	M	N	X	M
$Co(su)_4(ClO_4)_2$	14·8		7·7	14·9		7·9
$Co(su)_4(NO_3)_2$	20·2		8·5	20·7		8·7
$Co(su)_2Cl_2$	14·6	18·7	15·9	14·9	18·9	15·7
$Co(su)_2Br_2$	11·7	34·5	12·7	12·1	34·4	12·7
$Co(su)_3SO_4$	16·3		10·8	16·0		11·2
$Zn(su)_4(ClO_4)_2$	15·0		8·5	14·8		8·6
$Zn(su)_4(NO_3)_2$	20·8		9·6	20·6		9·6
$Zn(su)_2Cl_2$	14·3	18·9	17·2	14·7	18·6	17·1
$Zn(su)_2Br_2$	12·1	33·7	13·9	11·9	33·9	13·9
$Zn(su)_3SO_4$	15·2		12·1	15·8		12·3
$Cd(su)_2Cl_2$	12·8	16·2	26·2	13·1	16·5	26·2
$Cd(su)_2Br_2$	11·0	30·9	21·5	10·8	30·8	21·7
$Cd(su)_2I_2$	9·6	42·0	18·2	9·1	41·5	18·4
$Hg(su)Cl_2$	6·6	17·7		7·1	18·0	
$Hg(su)_2Cl_2$	11·1	13·6		10·8	13·7	
$Hg(su)_2Br_2$	9·1	26·5		9·2	26·3	
$Hg(su)_2I_2$	7·7	35·9		8·0	36·2	

Analytical data for the complexes are given in Table 1. All correspond stoicheiometrically to known thiourea complexes.[6-9] The cobalt(II) compounds were rather unstable and samples prepared for magnetic susceptibility determinations decomposed before any satisfactory results could be obtained. The complexes of the Group IIB elements were more stable and were not affected by periods of exposure to the atmosphere.

The deep blue-green cobalt(II) complexes have visible spectra characteristic of the tetrahedrally co-ordinated metal ion[11] (Table 2). The anion absorptions in the i.r. spectra of the cobalt and zinc perchlorate and nitrate complexes closely resemble one another and are very much as would be expected for species $M(su)_4A_2$ ($M =$ Co, Zn, $A = ClO_4^-$, NO_3^-, su = selenourea) containing tetrahedral $M(su)_4^{2+}$ and unco-ordinated perchlorate or nitrate ions[13] (Table 3). The appearance of a weakly i.r.-active perchlorate ν_1 vibration at 935 cm^{-1} is presumably due to a site-symmetry effect. The sulphato-complexes $Co(su)_3SO_4$ and $Zn(su)_3SO_4$ have spectra consistent with structures containing sulphate bound to the metal through one oxygen atom.[13]

The transitions in the visible spectra of the cobalt(II) complexes (Table 2) are classified on the assumption of T_d symmetry throughout, although the effective symmetry is lower than this even for the complexes containing the $Co(su)_4^{2+}$ ion (see below). The ligand field splitting ($10\,Dq$) and electronic repulsion term B were estimated graphically from plots of the transition energy ratios $\bar{\nu}_3/\bar{\nu}_2$ *versus* Dq/B and $E(\bar{\nu}_3)/B$ for an A_2 ground state of a tetrahedrally co-ordinated ion.[14] The energies of the transitions ${}^4T_1(F) \longleftarrow {}^4A_2$ ($\bar{\nu}_2$) and ${}^4T_1(P) \longleftarrow {}^4A_2$ ($\bar{\nu}_3$) were assumed to correspond to the centres of gravity of the multiple bands ν_2 and ν_3.

The data for the nitrate and perchlorate complexes yield average values of 4040 cm^{-1} for $10\,Dq$ and 0·61 for β, for the $Co(su)_4^{2+}$ ion. These compare with values[6] of 4250 cm^{-1} and 0·62 for $Co(tu)_4^{2+}$ (tu = thiourea), indicating that selenourea is slightly below thiourea in the spectrochemical series and has a similar very pronounced nephelauxetic effect. Additional estimates of

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[1] J. L. Duncan, *Spectrochim. Acta*, 1971, **27A**, 1197.

[2] G. B. Aitken, J. L. Duncan, and G. P. McQuillan, *J. Chem. Soc.* (*A*), 1971, 2695.

[3] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 1575.

[4] R. Rivest, *Canad. J. Chem.*, 1962, **40**, 2234.

[5] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527.

[6] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.

[7] C. D. Flint and M. Goodgame, *J. Chem. Soc.* (*A*), 1966, 744.

[8] D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1967, 884.

[9] I. Aucken, *Inorg. Synth.*, 1960, **6**, 26.

[10] P. J. Hendra and Z. Jovic, *Spectrochim. Acta*, 1968, **24A**, 1713.

[11] O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1249.

[12] A. T. Pilipenko and I. P. Sereda, *Zhur. neorg. Khim.*, 1961, **6**, 413.

[13] K. Nakomoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, London, 2nd edn., 1970.

[14] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, London, 1968.

10 Dq and B for $Co(su)_4^{2+}$ (given in parentheses in Table 2) were obtained from the spectra of the halide complexes $Co(su)_2Cl_2$ and $Co(su)_2Br_2$, by taking 10 Dq and B for chloride and bromide [15] to be the same as in $CoCl_4^{2-}$ and $CoBr_4^{2-}$ and using the average environment rule. The results are in satisfactory agreement with those previously obtained by Piovesana and Furlani [11] for the halide complexes. The sulphur bonded structures of the analogous thiourea complexes are well established and the close correspondence of the ligand field parameters for thiourea and selenourea confirms the underlying assumption that the selenourea ligands bind to the metal through the selenium atom.

TABLE 2

Visible absorption spectra [a] and ligand field parameters for cobalt(II) complexes

Compound	$^4T_1(F) \longleftarrow {}^4A_2$ ν_2 (cm^{-1})	$^4T_1(P) \longleftarrow {}^4A_2$ ν_3 (cm^{-1})	$\bar{\nu}_2$ (cm^{-1})	$\bar{\nu}_3$ (cm^{-1})	10 Dq (cm^{-1})	B' [c] (cm^{-1})	β
$Co(su)_4(ClO_4)_2$	7600 6000	14,800sh 13,200	7000	14,000	4030	575	0·59
$Co(su)_4(NO_3)_2$	7600 6400	15,600 12,600	6900	14,600	4050	620	0·63
$Co(su)_2Cl_2$ [b]	7500sh 6200 5300	15,800sh 15,000 13,000	6200	15,000	3650 (4200)	700 (660)	0·72 (0·68)
$Co(su)_2Br_2$ [b]	7800 6700 5800	15,000 14,200 13,300	6100	14,000	3450 (4050)	640 (560)	0·65 (0·58)
$Co(su)_3SO_4$	7400 6500 4800	14,900 13,400	6000	14,000	3500	640	0·65

[a] Data for Nujol mull spectra. [b] Figures in parentheses refer to 'hypothetical' $Co(su)_4^{2+}$ ion assuming 10 $Dq(CoX_4)^{2-}$ = 3100 and 2850 cm^{-1} for X = Cl, Br, and $B(CoX_4)^{2-}$ = 740 and 720 cm^{-1} for X = Cl and Br. [c] B For gaseous Co^{2+} = 976 cm^{-1}, $\beta = B'/976$.

TABLE 3

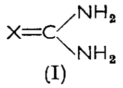
Infrared spectra of perchlorate, nitrate, and sulphate complexes

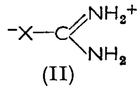
Perchlorates	ν_1	ν_3	ν_4
ClO_4^-	935 [a]	1100vs	630s
$Co(su)_4(ClO_4)_2$	935w	1100vs,br	625s
$Zn(su)_4(ClO_4)_2$	935w	1100vs,br	625s
Nitrates	ν_2	ν_3	ν_4
NO_3^-	831m	1390s	720
$Co(su)_4(NO_3)_2$	825m	1380s,br	*b*
$Zn(su)_4(NO_3)_2$	825m	1380s,br	*b*
Sulphates	ν_1	ν_3	ν_4
$SO_4^=$	983 [a]	1104	613
$Co(su)_3SO_4$	970m	1140s 1050s	640m 610m
$Zn(su)_3SO_4$	960s	1150s 1120sh 1030s	640m 615m

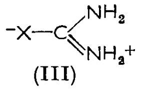
[a] Infrared inactive. [b] Overlaid by ligand absorption.

Infrared Spectra

Ligand Vibrations.—The structures of the diamides urea, thiourea, and selenourea may be represented by the canonical forms (I), (II), and (III) (X = O, S, and Se):


(I)


(II)


(III)

The C–N stretching force constants in urea, thiourea, and selenourea are 6·8, 7·5 and 7·6 mdyn Å^{-1} respectively,[2] indicating an increase in C–N bond order along the series. The $f_{OX}[(NH_2)_2CX] : f_{OX}(CX_2)$ ratio may be used as a measure of the CX bond order and yields approximate values of 0·7 (urea), 0·6 (thiourea), and 0·55 (selenourea). Clearly, contributions from structures (II) and (III) are important in selenourea and account for the very strong tendency of the ligand to co-ordinate through selenium rather than nitrogen. In the selenourea complexes the contributions from these structures should become even more predominant as the selenium electrons are involved in the co-ordinate bond, and this should be reflected in corresponding changes in the vibrational spectrum. These changes are not likely to be large: a crystal structure determination [16] for the complex $Te(su)_4Cl_2$ has revealed no significant alteration in the C–N or C–Se bond lengths, compared with those in the free ligand.[17]

The calculated potential energy distribution for the in-plane vibrations of selenourea is given in Table 4. The frequency ranges observed for the vibrations in selenourea complexes are included in Table 4. The C–N and C–Se stretching co-ordinates contribute to several of the normal modes and no single bands can be labelled unambiguously as 'C–N' or 'C–Se stretch'. Vibrations with a CN stretching contribution (ν_4, ν_5 and ν_{16}) do however tend to increase somewhat in frequency on co-ordination. The CSe stretching co-ordinate appears in ν_6 (640 cm^{-1}) but contributes principally to ν_7 (390 cm^{-1}). The frequency of ν_6 drops slightly (*ca.* 20 cm^{-1}) on co-ordination but ν_7 is very little changed. It is of course an oversimplification to consider the effect of co-ordination on the vibrations of the selenourea molecule only in terms of alterations in the CN and CSe force constants. The forms of the normal co-ordinates

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[15] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

[16] S. Hauge and M. Tysseland, *Acta Chem. Scand.*, 1971, **25**, 3072.

[17] J. S. Rutherford and C. Calvo, *Z. Krist.*, 1969, **128**, 229.

must be affected by the formation of the selenium–metal bond, and vibrations involving the C–Se bond in particular are unlikely to be directly comparable in the free and co-ordinated ligand. Metal–selenium stretching frequencies occur around 200 cm^{-1}, and any interaction with them would tend to increase the frequency of ligand vibrations having some carbon–selenium stretching character. Comparisons with the spectra of thiourea complexes are rather unhelpful as the distribution of the CS stretching co-ordinate in thiourea is not exactly like that for the CSe co-ordinate in selenourea. The CS stretch in thiourea appears mainly in ν_6 (732 cm^{-1}), which drops by *ca.* 30 cm^{-1} on co-ordination; the remainder is distributed almost equally between ν_4 (1415 cm^{-1}, 55% CN_2 sym. str.) and ν_7 (468 cm^{-1}, 60% CN_2 def.), neither of which seem to be very much affected by complex formation.[5]

TABLE 4

Calculated potential energy distribution for the planar vibrations of selenourea, and their frequency ranges in selenourea complexes [a] (calculated frequencies in parentheses)

	Observed Freq. (cm^{-1})	Frequency range in complexes [b] (cm^{-1})	$F_{1,1}$ NH_2 sym str.	$F_{2,2}$ NH_2 asym str.	$F_{3,3}$ CN_2 sym str.	$F_{4,4}$ CSe str.	$F_{5,5}$ NH_2 def.	$F_{6,6}$ NH_2 rock	$F_{7,7}$ CH_2 def.	$F_{3,4}$	$F_{3,5}$	$F_{3,6}$	$F_{3,7}$	$F_{4,7}$
ν_1	3320m (3348)	3450—3280		99·44				0·28	0·30					
ν_2	3250m [c] (3234)	3320—3200	99·58		0·40		0·14				−0·12			
ν_3	1610s (1611)	1660—1610 [d]	0·05	0·01	0·02	0·72	98·07	0·99	0·99	0·02	−0·70	0·02	0·01	−0·20
ν_4	1400s (1393)	1410—1400	0·17	0·25	51·51	14·87	8·10	30·92	23·10	−4·26	−10·21	−6·98	−3·00	−4·46
ν_5	1085w (1097)	1120—1090	0·14	0·19	37·43	1·81	0·40	54·95	0·09	−1·27	−1·93	7·93	0·16	0·10
ν_6	640m (639)	640—620	0·06	0·03	19·06	30·31	0·08	12·55	43·82	3·70	−0·61	−2·71	2·51	−8·77
ν_7	390s (386)	395—380		0·09	0·14	54·56		1·16	33·48	0·42	0·01	0·07	−0·19	10·28

			$F_{13,13}$ NH_2 sym	$F_{14,14}$ NH_2 asym str.	$F_{15,15}$ CN_2 asym str.	$F_{16,16}$ NH_2 def.	$F_{17,17}$ NH_2 rock	$F_{18,18}$ SCN_2 rock	$F_{15,16}$	$F_{15,18}$	$F_{17,18}$
ν_{13}	3320m (3351)	3450—3280		99·66			0·22	0·07			0·06
ν_{14}	3250m [c] (3232)	3320—3200	99·45		0·45	0·15			−0·06	−0·01	
ν_{15}	1610s (1612)	1660—1610 [d]	0·34		22·29	87·13	0·53	0·78	−9·45	−1·96	0·34
ν_{16}	1480m (1477)	1520—1500	0·14	0·05	71·39	13·50	7·60	7·71	6·66	−11·07	4·03
ν_{17}	1040vw (1037)		0·04	0·27	13·50	0·25	80·26	0·54	0·40	1·27	3·45
ν_{18}	340vw (344)	360—340	0·01	0·02	0·05	0·19	19·30	105·28	−0·02	−1·14	−23·72

[a] Derived from frequency data for [$^1H_4$]selenourea and [$^2H_4$]selenourea with force constants transferred as necessary from thiourea. [b] For details of individual spectra see G. B. Aitken, Ph.D. Thesis, Aberdeen, 1970. [c] Perturbed by Fermi resonance. [d] ν_3 And ν_{15} indistinguishable in spectra of complexes.

Many of the selenourea complexes also exhibit rather variable changes in the spectrum in the N–H stretching region, usually involving a sharpening of the band profiles and, in most cases, frequency increases of 0—100 cm^{-1}. Solid selenourea has a weakly hydrogen bonded structure,[17] and the breaking of these bonds on complex formation would be expected to produce the effects observed in the N–H stretching spectrum. The slight increase in the band frequency in the NH_2 deformation region probably arises through the contribution of the CN_2 asymmetric stretching vibration to the normal co-ordinate ν_{15}. The sulphato-complexes $Co(su)_3SO_4$ and $Zn(su)_3SO_4$ are exceptions to the general picture, having rather broad and poorly resolved N–H stretching absorptions at frequencies lower than those in the free ligand. These complexes presumably contain strong hydrogen bonds between the selenourea ligands and the unco-ordinated oxygen atoms of the sulphate groups.

Metal–Ligand Vibrations.—The available data on metal–selenium vibrations are not extensive[10,18,19] and refer mainly to platinum and palladium complexes.

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[18] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward Arnold, London, 1967.

[19] S. R. Allkins and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1325.

The assignments suggested for metal–selenium stretching vibrations cover rather a wide frequency range (150—316 cm^{-1}). The i.r. spectrum of solid selenourea is clear of absorption in this region and in fact contains only one band (at 138 cm^{-1}, presumably due to a lattice vibration) below 340 cm^{-1}.

Our assignments for M–Se and related stretching vibrations in the selenourea complexes are given in Table 5. The complexes containing the $M(su)_4^{2+}$ ion (M = Co or Zn) all exhibit three closely spaced bands which must be assigned to M–Se stretching modes. Although the local MSe_4 grouping may be expected to have T_d symmetry, giving rise to only one i.r.-active M–Se stretching mode, the M–Se–C bonds will not be collinear and the ion need not necessarily have overall tetrahedral symmetry. Site-symmetry effects may also interfere. Adams and Cornell[8] have observed similar effects in the spectra of the corresponding thiourea complexes and point out that the appearance of three i.r.-active M–S stretching vibrations is consistent only with symmetry not higher than D_2.

TABLE 5

Low frequency i.r. spectra of selenourea complexes

	ν(M–Se)	ν(M–X)	δ(M–Se–C) [a]
$Co(su)_4(ClO_4)_2$	245s 218m,sh 210s		142m
$Co(su)_4(NO_3)_2$	245s 224s 212m		165m,br
$Zn(su)_4(ClO_4)_2$	208s 196s 180s		
$Zn(su)_4(NO_3)_2$	202s 194m,sh 184s		
$Co(su)_2Cl_2$	213s 189w,sh	294s 288s,sh	174m
$Co(su)_2Br_2$	(246s, 218s, 211s,sh, 206s) [b]		140m
$Zn(su)_2Cl_2$	205s 180m,sh	270s,sh 266s	178m
$Zn(su)_2Br_2$	(206s,sh, 203s, 181m) [b]		156m
$Cd(su)_2Cl_2$	188s 165s,br	223s 204s	
$Cd(su)_2Br_2$	(181s, 173s, 151s, 142s) [b]		
$Cd(su)_2I_2$	167s,br	138m,sh 131s 123s?	
$Hg(su)_2Cl_2$	(204s, 200s,sh, 176s) [a]		
$Hg(su)_2Br_2$	(189m, 172s, 148s) [b]		
$Hg(su)_2I_2$	(155s,br, 126m,sh, 112m?) [a]		
$[Hg(su)Cl_2]_2$	183s,br	276s [c] 200s [d]	

[a] See text. [b] (νMSe + νMBr). [c] Terminal Hg–Cl. [d] Bridging Hg–Cl–Hg.

Hendra and Jovic[10] have assigned M–Se–C bending vibrations in the range 150—170 cm^{-1} for selenourea complexes of palladium(II) and platinum(II). Adams and Cornell[8] and Flint and Goodgame[7] discuss the assignment of bending vibrations in thiourea complexes and suggest frequencies around 200 and 140—150 cm^{-1} for M–S–C bending modes. The data are not entirely consistent, and it was necessary to postulate[8] very variable intensities for these absorptions in order to account for their non-appearance in some of the spectra. Several of our complexes contain bands in the 130—170 cm^{-1} region which may possibly arise from M–Se–C bending vibrations; here again the absorptions do not seem to occur consistently in the spectra of all the complexes and we must emphasise that the assignments to M–Se–C bending modes given in Table 5 are speculative.

The possible occurrence of M–Se–C bending absorptions around 150—160 cm^{-1} introduces complications into the interpretation of the spectra of those halide complexes which have M–Se or M–X stretching vibrations in the same frequency range. It seems reasonable to assume that in complexes with rather low M–Se stretching frequencies (specifically, those with cadmium and mercury halides) the bending vibration will also drop below its ' normal ' range, and the assignment of M–Se and M–X stretching vibrations is made on this basis. The assignment of separate metal–selenium and metal–halogen stretching vibrations is to some extent approximate as some interaction between the vibrations is to be expected. Metal–selenium and metal–bromine stretching vibrations in particular, will have very similar frequencies and separate assignments would be meaningless. The general trend in the metal–selenium stretching frequencies, decreasing in the order Co > Zn > Cd > Hg, is similar to that observed for metal–sulphur stretching frequencies in the corresponding thiourea complexes. The νMSe : νMS ratios for stretching vibrations in comparable selenourea and thiourea complexes fall in the range 0·74—0·82.

Mercury(II) halide complexes occur in a wide variety of structural types[20,21] and the interpretation of the spectra of the selenourea compounds consequently presents certain problems. The thiourea complex $Hg(tu)_2Cl_2$ has been shown by *X*-ray analysis[22] to contain planar trigonal (C_{2v}) ions $[Hg(tu)_2Cl]^+$ and chloride ions, but the i.r. spectrum is not simple and still awaits complete analysis.[8] If the selenourea complexes $Hg(su)_2X_2$ contain trigonal $[Hg(su)_2X]^+$ ions we would expect to observe three i.r.-active 'metal–ligand' stretching vibrations (approximately, 2M–Se + M–X). The bromide complex appears to be of this type, having three strong, well defined bands, assigned as 3(νMSe + νMBr) at 189, 172, and 148 cm^{-1}. The spectrum of the chloride complex also contains three strong absorptions in the metal–ligand stretching region, but it is rather more difficult to account for the observed frequencies. Metal–chlorine bond lengths in mercury(II) chloride complexes tend to vary considerably according to the nature of the other ligands in the mercury co-ordination sphere,[23] making the prediction of mercury–chlorine stretching frequencies a little difficult, but the bands at 204 and 200 cm^{-1} in $Hg(su)_2Cl_2$ certainly appear to belong

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[20] D. Grdenić, *Quart. Rev.*, 1965, **19**, 303.

[21] C-I. Branden, *Arkiv Kemi*, 1964, **22**, 501.

[22] K. K. Cheung, R. S. McEwen, and G. A. Sim, *Nature*, 1965, **205**, 383.

[23] K. K. Cheung and G. A. Sim, *J. Chem. Soc.*, 1965, 5988.

to mercury–chlorine stretching modes. Similarly, the single band at 176 cm^{-1} may reasonably be assigned to a mercury–selenium stretching vibration. This assignment is not consistent with a structure containing $[Hg(su)_2Cl]^+$ ions, or with a tetrahedral structure unless the band at 176 cm^{-1} is an unresolved doublet. If the complex does have the ionic structure extensive mixing of the skeletal vibrations must occur. The iodide complex appears to be similar to the chloride, although assignment of the low-frequency mercury–iodine stretching vibrations is complicated by the possibility of overlap with bending modes. *X*-Ray powder diffraction data indicate that $Hg(su)_2Br_2$ is isomorphous with $Hg(tu)_2Cl_2$, but that $Hg(su)_2Cl_2$ and $Hg(su)_2I_2$ are not.

The 1 : 1 complex $Hg(su)Cl_2$ has a spectrum consistent with a chlorine bridged dimeric structure, the terminal and bridging mercury–chlorine stretching vibrations having frequencies close to those found in chlorine-bridged dimeric complexes with phosphines, phosphine selenides and similar ligands.[24,25]

EXPERIMENTAL

The preparation of all the complexes was carried out in a nitrogen atmosphere.

Tetrakis(selenourea)metal(II) *Complexes*, $M(su)_4A_2$ (M = Co or Zn, A = ClO_4^- or NO_3^-.—A butanol solution of the appropriate hydrated metal salt (0·001 mol) was added dropwise to a refluxing solution of selenourea (0·004 mol) in butanol. The mixture was allowed to reflux for 30 min and left to cool. If precipitation did not occur on cooling light petroleum (60—80°) was added until a slight turbidity appeared, and the solution further cooled in an ice–salt bath for several hours. The solid product was washed with benzene and ether and dried *in vacuo*.

Sulphatotris(selenourea)metal(II) *Complexes*, $M(su)_3SO_4$ (M = Co or Zn).—An acetone–methanol solution of the hydrated metal sulphate (0·001 mol) was added to a refluxing solution of selenourea (0·004 mol) in acetone. Precipitation occurred almost immediately. The solid was washed with acetone and ether and dried *in vacuo*.

Dihalogenobis(selenourea)metal(II) *Complexes*, $M(su)_2X_2$ (*a*) M = Co or Zn; X = Cl or Br.—These complexes were obtained in the same way as the perchlorate and nitrate complexes using a 1 : 2 metal halide : selenourea ratio.

(*b*) M = Cd or Hg; X = Cl, Br, or I. A solution of the metal halide (0·001 mol) in acetone ($HgCl_2$, $HgBr_2$, and CdI_2) or ethanol ($CdCl_2$, and $CdBr_2$) was added to a refluxing solution of selenourea (0·002 mol) in acetone. (HgI_2 was added as a solid.) The $HgCl_2$ and $HgBr_2$ complexes precipitated as soon as the mole ratio HgX_2 : selenourea was 1 : 2, in the other cases it was necessary to allow the solutions to reflux for 30 min, cool, and add benzene to induce precipitation. The complexes were washed and dried as before.

$(Hg(su)Cl_2)_2$ Was obtained by adding selenourea (0·001 mol) in acetone to a solution of mercury(II) chloride. It is important to add the selenourea to the mercury(II) chloride solution, to avoid the formation of the 1 : 2 complex $Hg(su)_2Cl_2$.

Nickel(II) *Complexes*.—Attempts to prepare complexes with nickel(II) salts were unsuccessful. A bright green solid was obtained with nickel(II) bromide but this proved to be very unstable and decomposed before it could be fully characterised.

Thiourea Complexes.—These were prepared by standard methods.[6-9] Cotton, Faut, and Mague [6] remark that on one occasion during the preparation of $Co(tu)_3SO_4$ in methanol solution an unidentified green product also crystallised. A similar compound crystallises readily from ethanol solution and is a mixed-ligand complex $Co(tu)_3SO_4,2EtOH$ (Found: C, 16·8; H, 4·6; N, 18·0. Calc. for $C_7H_{24}CoN_6O_6S_4$: C, 17·6; H, 5·0; N, 17·6%). The complex loses ethanol quantitatively at 80 °C to form blue $Co(tu)_3SO_4$. (Weight loss found, 19·3%; calc., 19·3%). The methanol complex is rather less stable than the ethanol complex and loses methanol more rapidly under ambient conditions. The tetrahedral complex $Co(tu)_3SO_4$, once formed, shows no tendency to recombine with methanol or ethanol.

I.r. spectra were obtained using Perkin-Elmer 457 and 225 and RIIC FS620 spectrophotometers. The far-i.r. spectra (<200 cm^{-1}) were computed to an effective resolution of 4 cm^{-1}. Visible spectra were measured for Nujol mulls using a Unicam SP 700 spectrophotometer. *X*-Ray powder diffraction data were obtained with a Phillips PW1051 powder diffractometer with Cu-K_α radiation.

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