

# Hydration Behaviour of Some Alkyl Dithiocarbonates and Their Mixed-ligand Oxalatochromate Complexes\*

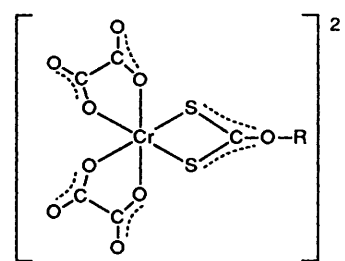
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A series of mixed-ligand chromate complexes,  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  ( $ox = \text{oxalate}$ ,  $R = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i, \text{Bu}^s \text{ or } \text{CH}_2\text{Ph}$ ), has been isolated and characterized. From density and ultrasonic velocity measurements at 25, 35 and 45 °C of the potassium salts  $K[S_2COR]$  of the alkyl dithiocarbonates and their corresponding mixed-ligand chromate complexes in aqueous solution, partial molal volumes ( $V_2^0$ ), partial molal adiabatic compressibilities ( $\kappa_2^0$ ) and hydration numbers ( $n_H$ ) have been determined. The hydration atmospheres around the second co-ordination sphere of the complexes in solution have been examined as a function of temperature. The results have been interpreted in terms of differences in hydration behaviour of the ligands and complexes, on the basis of known hydration models.

The co-ordination of water outside the first co-ordination sphere (f.c.s.) in an aqueous solution, referred to specifically as outer-sphere hydration, has long been a subject of study in connection with metal complex-ion equilibria.<sup>1</sup> The second co-ordination sphere (s.c.s.) displays a type of organization different from that in the bulk solvent and is dictated in part by its proximity to the metal ion and its f.c.s. Studies have already been undertaken to investigate the nature of the linkage between the ligands in the f.c.s. and in the s.c.s. In fact, the s.c.s. can be viewed as a linking zone between the co-ordinated ion and bulk solvent.<sup>3a</sup>

The use of complex species to study ion-water interactions<sup>4,5</sup> is advantageous as the ligands in the co-ordination sphere can be changed in such a way as to effect a variation in molecular size or charge, or both. We have prepared a series of water-soluble mixed-ligand chromate complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$ , where  $ox$  is the bidentate dianion of oxalic acid and  $S_2COR$  is a bidentate monoanionic alkyl dithiocarbonate, and undertaken a study of the hydration numbers  $n_H$  of these complexes as well as those of  $K[S_2COR]$ . We are then able to investigate the influence of chain length and structural complexities towards the s.c.s. Until recently dipolar compounds such as amino acids, quaternary ammonium or phosphonium salts were used in the study of solute-solvent interactions. In such species the polar region of the molecule causes electrostriction and their non-polar region shows hydrophobic hydration.<sup>6</sup> However, these compounds suffer from the disadvantage that on increasing the size and complexity of the non-polar groups, their solubility in aqueous media is diminished significantly. The compounds reported herein consist of a doubly charged complex anion with a non-polar organic group (R) protruding outwards and away from the spherical co-ordination sphere of the metal ion and offer scope for studying the effect of variation of chain length and structure on electrostriction as well as on hydrophobic hydration. Similar complexes with longer and more complex chains will be of interest as they can mimic certain types of macromolecules and surfactants. In this paper we report our findings on the partial molal characteristics and hydration numbers of the salts  $K[S_2COR]$  and the mixed-ligand complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  ( $R = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i, \text{Bu}^s \text{ or } \text{CH}_2\text{Ph}$ ).



## Experimental and Theory

Solution conductivity measurements were made using a Systronics digital conductometer (model 304). Thermogravimetry and differential thermal analysis were carried out on a Simadzu DT 30 thermal analyser. Solid-state magnetic data were obtained with an EG and G PAR vibrating-sample magnetometer (model 155) and ESR spectra were run at liquid-nitrogen temperature on a Varian E-112 X/Q-band spectrometer at the Regional Sophisticated Instrumentation Centre, Madras. Electronic spectra of samples (as Nujol mulls) were obtained on a Pye-Unicam SP8-150 spectrometer. X-Ray powder diffraction patterns were obtained courtesy of the Department of Geology, Jadavpur University, Calcutta on a Philips XRD diffractometer (PW 1730/1710) kept in a room at 3020 relative humidity, using  $\text{Cu-K}\alpha$  radiation. Infrared spectra were measured on a Perkin-Elmer 983 spectrophotometer.

*Synthesis of the Complexes.*—The parent complex  $cis-K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$  was prepared by a standard method<sup>7</sup> and its composition checked.<sup>7</sup> The potassium salts  $K[S_2COR]$  of the *O*-alkyl dithiocarbonates were prepared following the procedure described in ref. 8 with necessary modifications. Each compound was recrystallised from light petroleum (b.p. 40–60 °C) and the purity checked by determining the sulfur content gravimetrically.<sup>9</sup> Each of the complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  was prepared by mixing  $cis-K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$  and  $K[S_2COR]$  (1:1) in a fixed volume of water so as to make the solution 0.25 molal in the resultant complex. The mixture was shaken well and equilibrated for 30 min at 45 °C in a constant-temperature bath. The solution was then slowly evaporated at room temperature. The dark green crystals thus obtained were collected and washed repeatedly with light petroleum (b.p. 40–60 °C) in which  $K[S_2COR]$  were readily

\* Non-SI units employed: bar =  $10^5$  Pa, G =  $10^{-4}$  T.

**Table 1** Analytical, magnetic and electronic (mull) spectral data of complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$ 

Compound	Found (calc.) (%)			$\mu_{eff}$	$\lambda_{max}/nm$
	Oxalate	Cr	S		
$K_2[Cr(ox)_2(S_2COMe)] \cdot 3H_2O$	37.80 (37.65)	10.95 (11.10)	13.20 (13.70)	4.39	410, 565, 690
$K_2[Cr(ox)_2(S_2COEt)] \cdot 2H_2O$	38.10 (38.00)	11.10 (11.20)	13.30 (13.80)	4.34	410, 565, 690
$K_2[Cr(ox)_2(S_2COPr^i)] \cdot 2H_2O$	37.10 (36.85)	10.90 (10.90)	13.10 (13.40)	4.31	410, 565, 690
$K_2[Cr(ox)_2(S_2COPr^i)] \cdot 2H_2O$	37.00 (36.85)	10.70 (10.90)	13.10 (13.40)	4.23	410, 565, 690
$K_2[Cr(ox)_2(S_2COBu^n)] \cdot 2H_2O$	36.00 (35.80)	10.50 (10.55)	12.25 (13.00)	4.36	410, 565, 690
$K_2[Cr(ox)_2(S_2COBu^i)] \cdot 2H_2O$	36.00 (35.80)	10.70 (10.55)	12.10 (13.00)	4.32	410, 565, 690
$K_2[Cr(ox)_2(S_2COBu^i)] \cdot 2H_2O$	36.10 (35.80)	10.60 (10.55)	12.15 (13.00)	4.36	410, 565, 690
$K_2[Cr(ox)_2(S_2COCH_2Ph)] \cdot H_2O$	34.90 (34.70)	10.10 (10.25)	12.35 (12.60)	4.35	410, 565, 690

**Table 2**  $d$  Spacings (Å) of some strong lines from the X-ray powder diffraction patterns of *cis*- $K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$  **1** and  $K_2[Cr(ox)_2(S_2COR)]$  (R = Et, **2**; Bu<sup>n</sup>, **3**; Bu<sup>i</sup>, **4**; or Bu<sup>t</sup>, **5**)

1	2	3	4	5
—	—	—	16.97	—
—	12.26	12.26	12.26	12.26
—	8.18	8.18	8.35	8.41
—	—	—	—	—
6.64	6.90	6.85	—	—
6.55	6.59	6.59	—	—
6.18	—	—	—	—
5.93	5.97	5.97	5.89	5.89
5.53	5.53	5.53	5.53	5.46
—	5.27	5.27	5.27	—
4.84	4.94	4.94	4.92	—
4.66	4.76	4.76	4.71	4.71
4.47	—	—	—	—
4.30	4.36	4.34	4.34	4.32
4.16	—	—	—	—
—	4.03	4.03	—	—
3.91	—	—	—	—
3.76	—	—	—	—
3.61	3.67	3.65	3.67	3.64
3.51	—	—	—	—
3.44	—	3.42	3.42	3.42
3.37	—	—	—	—
3.23	3.25	3.27	3.28	3.22
3.19	—	—	—	—
3.05	—	—	—	—

soluble. The product  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  was filtered off by suction and the resulting shiny dark green crystals stored in a vacuum desiccator over silica gel. Table 1 lists the analytical, magnetic, and electronic spectral data and Table 2 X-ray powder diffraction data for some of the compounds.

**Apparatus and Measurements for Solution Studies.**—The densities and ultrasonic sound velocities of solutions were measured at 25, 35 and 45 °C with calibrated Ostwald-Sprengel type pycnometers (25 cm<sup>3</sup> capacity) and an ultrasonic interferometer operating at 5 MHz (model m-82, Mittal, India) respectively. The temperature was kept constant ( $\pm 0.02$  °C) with the aid of a thermostat arrangement in a constant-temperature water-bath. The average uncertainties in the density and sound velocity determinations were  $\pm 1 \times 10^{-5}$  g cm<sup>-3</sup> and  $\pm 0.5$  m s<sup>-1</sup> respectively. Deionised water was doubly distilled in all-glass apparatus and degassed before use.

The measured density and sound velocity data were used to calculate the apparent and partial molal volumes [ $V_{app}$  and  $V_2^0$  (cm<sup>3</sup> mol<sup>-1</sup>)] and adiabatic compressibilities [ $\kappa_{s,app}$  and  $\kappa_s^0$  (cm<sup>3</sup> mol<sup>-1</sup> bar<sup>-1</sup>)] and the hydration numbers ( $n_H$ ). The apparent molal volume  $V_{app}$  can be obtained from equation (1)

$$V_{app} = \frac{1000}{mdd_1} (d_1 - d) + M_2/d \quad (1)$$

where  $m$  is the molality of the solute (mol kg<sup>-1</sup>),  $d$  and  $d_1$  are

the densities (g cm<sup>-3</sup>) of the solution and pure solvent respectively and  $M_2$  the molar mass of the solute. The partial molal volume can be described by either the Masson or Redlich–Meyer equations [(2) and (3) respectively], where  $S'_v$  is the

$$V_{app} = V_2^0 + S'_v m^{\frac{1}{2}} \quad (2)$$

experimental slope,  $B_v$  the empirical deviation constant and  $S_v$

$$V_{app} = V_2^0 + S_v m^{\frac{1}{2}} + B_v m \quad (3)$$

the theoretical slope. Values of  $V_2^0$  at 25 °C obtained from the Redlich–Meyer equation are given in parentheses in Table 3. At other temperatures the Masson equation was employed for the salts and the uncertainty in  $V_2^0$  was  $\pm 0.1$ – $0.2$  cm<sup>3</sup> mol<sup>-1</sup>.

The adiabatic compressibility  $\beta_s$  (bar<sup>-1</sup>) was evaluated using the Laplace equation (4), where  $u$  is the sound velocity in m s<sup>-1</sup>.

$$\beta_s = 100/u^2 d \quad (4)$$

The apparent molal adiabatic compressibilities were calculated using equation (5) where  $\beta_s$  and  $\beta_{s,1}$  are the

$$\kappa_{s,app} = \frac{1000(\beta_s - \beta_{s,1})}{md_1} + \beta_s V_{app} \quad (5)$$

compressibilities of the solution and pure solvent respectively.

The concentration dependence of  $\kappa_{s,app}$  can be described by equation (6) where  $S'_{\kappa_s}$  is the experimental slope.<sup>4</sup> The uncertainty in  $\kappa_s^0$  is  $1 \times 10^{-4}$ – $1.5 \times 10^{-4}$  cm<sup>3</sup> mol<sup>-1</sup> bar<sup>-1</sup>.

$$\kappa_{s,app} = \kappa_s^0 + S'_{\kappa_s} m^{\frac{1}{2}} \quad (6)$$

The concentration dependence of  $\kappa_{s,app}$  can be described by equation (7) where values of  $S_{\kappa_s}$  can be determined from the

$$\kappa_{s,app} = \kappa_s^0 + S_{\kappa_s} m^{\frac{1}{2}} + \beta_{\kappa_s} m \quad (7)$$

Debye–Hückel slope. However it is not possible to determine  $\kappa_s^0$  by plotting  $\kappa_{s,app} - S_{\kappa_s} m^{\frac{1}{2}}$  against molality as the values of the limiting slope calculated from the data are those obtained under isothermal conditions.<sup>10</sup> Lack of sufficient thermodynamic data precludes the estimation of the limiting slopes under adiabatic conditions; however, the values of the limiting slopes under adiabatic and isothermal conditions seem to be of similar magnitude and differ by only ca. 10%. Therefore it is convenient to express the concentration dependence<sup>4a</sup> of  $\kappa_{s,app}$  in terms of equation (6).

The hydration numbers  $n_H$  were calculated from equation (8) after Surdo and Millero,<sup>11</sup> where  $\bar{\kappa}_{s,1}^0(\text{elect})$  (cm<sup>3</sup> mol<sup>-1</sup>

$$n_H = -\bar{\kappa}_{s,1}^0(\text{elect})/\beta_{s,1} \bar{V}_{1,B}^0 \quad (8)$$

bar<sup>-1</sup>) is the partial molal compressibility due to electrostriction and practically equal to  $\kappa_s^0$ ,  $\beta_{s,1}$  and  $\bar{V}_{1,B}^0$  are the compressibility of pure water and molar volume of the bulk water respectively.

**Table 3** Partial molal volumes  $V_2^\circ$  ( $\text{cm}^3 \text{mol}^{-1}$ ), partial molal adiabatic compressibilities  $\kappa_2^\circ$  ( $\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$ ) and hydration numbers  $n_H$ 

$T/^\circ\text{C}$	$V_2^\circ$			$10^4 \kappa_2^\circ$			$n_H$		
	25	35	45	25	35	45	25	35	45
<b>K[S<sub>2</sub>COR]</b> R = Me	80.0 (81.0)*	80.6	81.2	-59	-55	-50	7.2	6.9	6.4
Et	90.0 (95.5)	91.2	96.6	-61	-52	-45	7.5	6.5	5.7
Pr <sup>n</sup>	110.2 (112.0)	114.8	119.2	-67	-62	-56	8.2	7.8	7.1
Pr <sup>i</sup>	101.8 (106.0)	105.8	108.4	-68	-61	-55	8.4	7.7	7.0
Bu <sup>n</sup>	120.2 (126.5)	123.4	128.6	-70	-60	-58	8.6	7.5	7.4
Bu <sup>i</sup>	121.4 (127.5)	127.0	129.0	-80	-72	-65	9.8	9.0	8.3
Bu <sup>s</sup>	136.0 (141.0)	136.6	142.6	-62	-45	-41	7.6	5.6	5.2
CH <sub>2</sub> Ph	146.2 (147.5)	150.0	153.0	-58	-38	-36	7.1	4.8	4.6
<b>K<sub>2</sub>[Cr(ox)<sub>2</sub>(S<sub>2</sub>COR)]·xH<sub>2</sub>O</b> R = Me	212.0 (217.5)	220.0	235.0	-117	-106	-90	14.4	13.4	11.5
Et	204.5 (214.0)	205.2	210.0	-100	-96	-92	12.3	12.1	11.2
Pr <sup>n</sup>	216.0 (225.0)	222.4	235.8	-96	-89	-87	11.8	11.2	11.1
Pr <sup>i</sup>	226.4 (234.0)	238.6	241.6	-94	-78	-62	11.6	9.8	7.9
Bu <sup>n</sup>	242.4 (248.0)	250.0	270.4	-95	-90	-83	11.7	11.3	10.6
Bu <sup>i</sup>	246.0 (250.0)	251.2	264.2	-97	-87	-67	11.9	10.9	8.5
Bu <sup>s</sup>	255.4 (257.5)	261.2	262.0	-95	-85	-78	11.7	10.7	10.0
CH <sub>2</sub> Ph	246.4 (251.0)	262.0	262.6	-109	-97	-67	13.4	12.2	8.5

\* Values in parentheses refer to the Debye-Hückel correction in terms of equation (3) at 25 °C. Values of  $V_2^\circ$  and  $\kappa_2^\circ$  for the corresponding ions  $[\text{S}_2\text{COR}]^-$  and  $[\text{Cr}(\text{ox})_2(\text{S}_2\text{COR})]^{2-}$  obtained using  $V_2^\circ(\text{K}^+) = 3.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $\kappa_2^\circ(\text{K}^+) = -26.5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$  at 25 °C. The  $V_2^\circ$  and  $\kappa_2^\circ$  values for *cis*-K[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O are 158.5 cm<sup>3</sup> mol<sup>-1</sup> and  $-63.0 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$  and the corresponding values of the anion are 155.2 cm<sup>3</sup> mol<sup>-1</sup> and  $-36.5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$  respectively.

It should be mentioned that equation (8) has been used with our ultrasonic data representing adiabatic compressibilities although strictly it relates to isothermal conditions.<sup>3b</sup> Desnoyers and Philip<sup>12</sup> derived a convenient equation for the conversion of adiabatic to isothermal compressibilities and Mathieson and Conway<sup>10</sup> have shown that the differences between the values obtained are small and should not significantly effect the hydration number determined by equation (8).

To obtain the anionic contribution to  $V_2^\circ$  and  $\kappa_2^\circ$ , the corresponding values for K<sup>+</sup> were subtracted (using  $V_2^\circ = 3.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $\kappa_2^\circ = -26.5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$  at 25 °C reported by Kawaizumi *et al.*<sup>4a</sup> as taken from the data tabulated by Millero<sup>13</sup> and Mathieson and Conway<sup>10</sup>). Values of  $V_2^\circ$  of the ions at 25 °C were obtained from the data in parentheses in Table 3 relating to the partial molal volumes  $V_2^\circ$  as calculated from the Redlich-Meyer equation.

## Results and Discussion

**Composition of the Complexes.**—Chromium, sulfur and oxalate contents of the mixed-ligand chromate complexes were determined by volumetric and gravimetric methods.<sup>8,9</sup> The results were in accord with the formulae K<sub>2</sub>[Cr(ox)<sub>2</sub>(S<sub>2</sub>COR)]·xH<sub>2</sub>O (Table 1).

The formulae of the prepared complexes were then confirmed by carrying out conductance measurements on mixing *cis*-K<sub>2</sub>[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O and K[S<sub>2</sub>COR] in proportions laid

down by the principles of slope-ratio and Job's method.<sup>14</sup> In each case a sharp break in the conductivity corresponding to the formation of a 1:1 species was observed.

**Lattice Water.**—Thermogravimetry shows a weight loss at *ca.* 100–150 °C, accompanied by an endotherm in the DTA curves, due to loss of water molecules in all the complexes studied.

**Magnetic Moments, ESR and Electronic Spectra.**—The magnetic moments of the complexes K<sub>2</sub>[Cr(ox)<sub>2</sub>(S<sub>2</sub>COR)]·xH<sub>2</sub>O as well as of *cis*-K[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O and K<sub>3</sub>[Cr(ox)<sub>3</sub>] are slightly higher than expected for a spin-free d<sup>3</sup> system (Table 1). The ESR spectra for the methyl or ethyl dithiocarbonate complexes show *g* values of 2.01 and 2.02 respectively (scan range 4000 G with the magnetic field set at 3300 G). For the remaining complexes very weak signals at low and high fields were also observed in addition to a prominent signal very close to that of diphenylpicrylhydrazyl (*g* = 2.00), indicating distortion from cubic symmetry.

Analysis of the magnetic data, ESR and electronic spectra for solid samples indicates that the chromium is in the 3+ oxidation state in the mixed-ligand complexes. The electronic transitions in the UV/VIS region observed are  ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ ,  ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$  and  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}$  corresponding to a d<sup>3</sup> octahedral ion. A shoulder at 14 492 cm<sup>-1</sup>, indicative of the spin-forbidden transition  ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$  could also be ob-

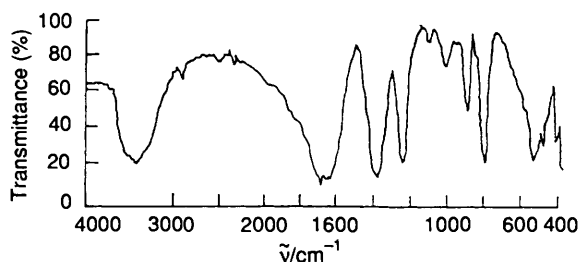


Fig. 1 Infrared spectrum of  $K_2[Cr(ox)_2(S_2COBu^n)] \cdot 2H_2O$

served. The  $10Dq$  value of these compounds was found to be  $17699\text{ cm}^{-1}$  and the Racah parameter ( $B$ )  $662.8\text{ cm}^{-1}$ . Considering the free-ion value for  $B$  of  $918\text{ cm}^{-1}$ , the nephelauxetic ratio is 0.722. This can be compared to the value of 0.692 for  $cis\text{-}K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$  suggesting that the delocalization of the metal-based electrons onto the molecular orbitals of the dithiocarbonate ligand is less effective than onto the co-ordinated water indicating that the latter shows stronger  $\sigma$  bonding. The formation of the mixed-ligand dithiocarbonate complexes  $K_2[Cr(ox)_2(S_2COR)]$  is thus presumably entropy driven (chelate effect).

**X-Ray Diffraction Patterns.**—All the dithiocarbonatochromate complexes have similar diffraction patterns which differ from the parent complex  $K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$ . The 'd spacings' for the complexes are very similar suggesting that they are isostructural (Table 2).

**Infrared Spectra.**—As expected, the IR spectra of the mixed-ligand complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  show many overlapping bands. Each compound (a representative spectrum, that of  $K_2[Cr(ox)_2(S_2COR)] \cdot 2H_2O$  is given in Fig. 1) shows a broad band at  $3000\text{--}3500\text{ cm}^{-1}$  due to lattice water, arising from antisymmetric and symmetric OH stretches. A small but significant peak at  $3500\text{ cm}^{-1}$ , indicative of a free OH stretch of the co-ordinated water, was also observed for  $cis\text{-}K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$ . In the region  $1600\text{--}1700\text{ cm}^{-1}$  several peaks were observed with HOH bending modes merged with  $\nu(C=O)$  for oxalate. In the region  $2800\text{--}2900\text{ cm}^{-1}$  the salts  $K[S_2COR]$  except for the methyl derivative show several peaks, indicative of C-H stretches of the R group.<sup>15</sup> For the complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  these peaks are separated into three weak bands at  $2900$ ,  $2800$  and  $2500\text{ cm}^{-1}$ .

All the complexes show a conspicuous strong band at  $1400\text{ cm}^{-1}$  due to  $\nu(C=O)$  and  $\nu(C-C)$  of the oxalato group,<sup>16</sup> as well as a combination band of two other weak bands; one slightly above  $1400\text{ cm}^{-1}$  due to methylene group(s) the other slightly below  $1400\text{ cm}^{-1}$  due to the terminal methyl group of the hydrocarbon chain. The complexes also show a strong combination band in the region  $1255\text{--}1260\text{ cm}^{-1}$  due to  $\nu(CO) + \delta(O-C=O)$  and  $\nu(C-S)$ .<sup>16-18</sup> For the salts  $K[S_2COR]$  this band is very weak.

The *O*-alkyl dithiocarbonate ligands are characterized by a number of strong bands between  $1000$  and  $1200\text{ cm}^{-1}$  involving O-C and C-S bonds.<sup>15,19</sup> In the resulting complexes, some of these peaks merge to a single strong band. This is due to delocalization of  $\pi$  bonds, whereby the two C-S bonds are made nearly equivalent in the resulting complexes.

The complexes show a sharp combination band at  $900\text{ cm}^{-1}$ , due to  $\nu(OC) + \nu(O-C=O)$  as found also in  $K[Cr(ox)_2(S_2COR)] \cdot 2H_2O$ . A band at  $810\text{ cm}^{-1}$  is due to  $\delta(O-C=O) + \nu(M-O)$  which is shifted to  $820\text{ cm}^{-1}$  for  $cis\text{-}K[Cr(ox)_2(H_2O)_2] \cdot 2H_2O$ . All the complexes show a strong broad band at  $\approx 550\text{ cm}^{-1}$  due to  $\nu(C-S)$ . The  $\delta(C-O-C)$  band of the dithiocarbonate ligands at  $\approx 450\text{ cm}^{-1}$  is shifted for the resulting complexes to  $415\text{ cm}^{-1}$  which coincides with the band indicative of  $\nu(M-O) +$  ring deformation of the oxalato group. The

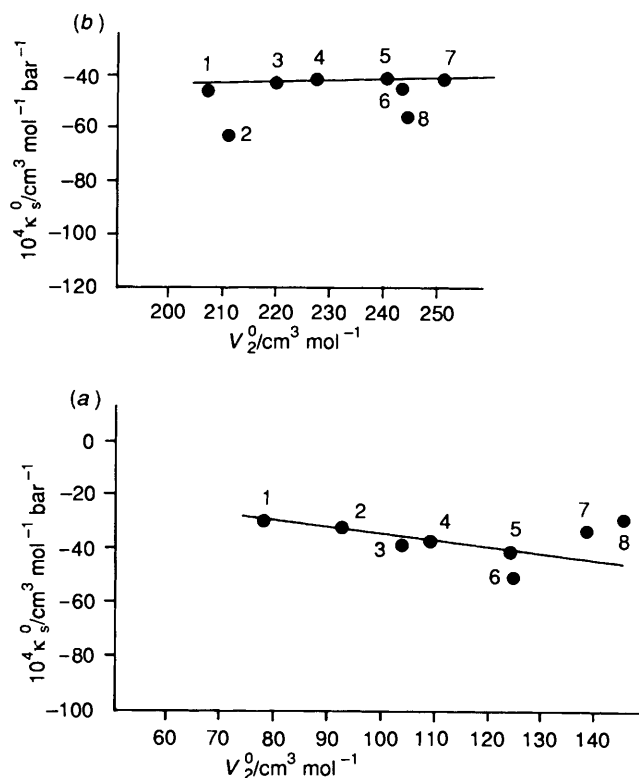


Fig. 2 Relationship between values of  $\kappa_s^0$  and  $V_2^0$  for (a) ions  $[S_2COR]^-$  and (b)  $[Cr(ox)_2(S_2COR)]^{2-}$ : R = Me, 1; Et, 2; Pr<sup>n</sup>, 3; Pr<sup>i</sup>, 4; Bu<sup>n</sup>, 5; Bu<sup>i</sup>, 6; Bu<sup>t</sup>, 7; and CH<sub>2</sub>Ph, 8

chromium-sulfur  $\sigma$  bond shows a broad weak band at  $\approx 350\text{ cm}^{-1}$  (not shown in Fig. 2) is due to  $\nu(M-S)$ .

**Hydration Behaviour.**—The partial molal volumes  $V_2^0$  of the dithiocarbonatochromate complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$  and of the salts  $K[S_2COR]$  increase with increase in temperature (Table 3). At higher temperatures, the hydrophobic hydration and electrostriction of the solvent decreases and the intrinsic size of the solute increases due to thermal expansion so leading to increases in  $V_2^0$ . For  $K[S_2COMe]$  the methyl group undergoes weaker hydrophobic hydration,<sup>4c</sup> and therefore contributes less to the volume changes. A comparison of  $V_2^0$  among the ligands with isomeric alkyl groups show that, although there is a marked variation in  $V_2^0$  values, they do not follow any regular sequence.<sup>20</sup> From the  $V_2^0$  values obtained [from equation (3) and given in parentheses in Table 3] we can compute the  $V_2^0$  values of the respective ions  $[S_2COR]^-$  and  $[Cr(ox)_2(S_2COR)]^{2-}$  at  $25^\circ\text{C}$ .

The volume changes ( $\Delta V_2^0$ ) associated with complex formation at  $25^\circ\text{C}$  can be obtained from equation (9) and an

$$\Delta V_2^0 = V_2^0[Cr(ox)_2(H_2O)_2]^- + V_2^0[S_2COR]^- - V_2^0[Cr(ox)_2(S_2COR)]^{2-} \quad (9)$$

average value of  $38.5\text{ cm}^3\text{ mol}^{-1}$  is obtained. This value indicates that two molecules of water are replaced during complex formation. For the methyl and benzyl dithiocarbonato complexes, deviation of  $\Delta V_2^0$  from this average value may be explained from the fact that, apart from complexing water molecules, the secondary solvation of ions for these complexes seems to be altered during complex formation. Significantly the lattice water of the crystalline compounds of these two complexes also differs. Alteration of secondary solvation on complex formation is also supported from the variation of  $n_H$  with temperature (Table 3). The partial molal adiabatic compressibilities ( $\kappa_s^0$ ) of the salts  $K[S_2COR]$  and as the complexes increases with increasing temperature (Table 3). This

may be explained on the basis of reduced translational immobilization, rupture of hydrogen bonds of the structured (so-called microscopic icebergs) water molecules oriented due to hydrophobic hydration around R and thermal destabilization of the electrostricted zone which make the system more accessible to compression; the higher negative values for the methyl and benzyl dithiocarbonato mixed-ligand complexes are due to high electrostriction which reduces the significance of the hydrophobic hydration.

The contributions of the *O*-alkyl dithiocarbonato ligands to  $V_2^\circ$  and  $\kappa_s^\circ$  alter upon co-ordination to the metal ion. For the free ligands  $[S_2COR]^-$ , a linear relationship has been found between  $\kappa_s^\circ$  and  $V_2^\circ$  for linear-chain alkyl dithiocarbonates [Fig. 2(a)]. The negative slope with increasing  $V_2^\circ$  indicates increasing hydrophobic structure-making behaviour with increase in chain length. The electron density is delocalized on the S-C-S bonds and is stabilized through resonance. The charge is localized on this part of the ion and it is expected that the electrostriction at this site does not have much scope to influence the hydrophobic hydration exhibited by the alkyl group, as has been depicted schematically by Marcus for the butanoate anion in water.<sup>3c</sup> For the complexes  $K_2[Cr(ox)_2(S_2COR)] \cdot xH_2O$ , the hydrophobicities of the structure-making groups are masked by the electrostriction caused by the uniform charge distribution<sup>4</sup> over the entire complex ions. Thus there is almost no variation of  $\kappa_s^\circ$  with  $V_2^\circ$  [Fig. 2(b)].

Whether such a model of uniform charge distribution on the periphery of the complex is maintained on increasing the chain length or complexity of the hydrocarbon will be an interesting study for the future.

#### Acknowledgements

Support of this work by the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. The authors thank the Head, Department of Geology, Jadavpur University, Calcutta for providing X-ray patterns and Dr. S. Koner, Inorganic Chemistry Department, Indian Association for the Cultivation of Science, Calcutta, for extending his assistance towards obtaining thermal data.

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Received 15th August 1991; Paper 1/04282C