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Reaction Entropies of Redox Reactions of Transition-Metal Complexes with Sulfur Donor Ligands

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The reaction entropy, $\Delta S_{ex}°$, of redox reactions of transition-metal dithiocarbamato complexes, $M(R_2dtc)_x$ (M = Ni, Cu, Pd, Fe, Mn, Co, W, Mo; R = alkyl, benzyl; x = 2–4), and some related complexes is determined in the nonaqueous solvents acetone, acetonitrile, and dimethyl sulfoxide. The differences found between the experimental data and the predictions obtained from simple electrostatic models are ascribed to (a) the particular charge distribution in the $M(R_2dtc)_x$ complexes and (b) the stereochemistry of the solvent dipoles. Because a $M(R_2dtc)_x$ complex often shows more than one reversible redox reaction, it is possible to use a relative form of the Born formula in the calculation of effective ionic radii in solution. These effective radii were found to be in good agreement with crystallographic radii. The possible influence of the substituent R and $E°$ upon $\Delta S_{ex}°$ is discussed.

Introduction

Reaction entropy data are well suited to study in detail solvent changes accompanying electron-transfer reactions.[1-4] Recently, the conclusion was reached that for mixed-valence metal complexes the extent of the polarized solvent layer consists of only a few molecules.[5] Another group of coordination complexes, which is interesting for the study of reaction entropies, is the chemically and electrochemically well-studied transition-metal dithiocarbamato complexes $M(R_2dtc)_x$.[6-9] With the dtc ligand a class of complexes can be synthesized in which there is a large variation of the central metal atom, the coordination number, the formal oxidation state of the metal, and the substituent R. It is well documented that the dtc complexes studied here, i.e. bis complexes $M(R_2dtc)_2$ (M = Cu,[10,11] Ni,[10,12] Pd[13]), tris complexes $M(R_2dtc)_3$ (M = Fe,[14,15] Mn,[16] Co[17-19]), and tetrakis complexes $M(R_2dtc)_4^+$ (M = Mo,[20,21] W[20,21]), undergo reversible one-electron-transfer reactions according to eq 1 and 2. The half-wave potentials of these redox reactions comprise a wide range of values (−1.4 to +1.3 V vs. Ag/AgCl).

$$M(R_2dtc)_x^{z} \rightleftharpoons M(R_2dtc)_x^{z+1} + e^- \qquad (1)$$

$$e^- + M(R_2dtc)_x^{z} \rightleftharpoons M(R_2dtc)_x^{z-1} \qquad (2)$$

This large variety in molecular parameters enables us to trace the influence of the radius and the charge of the complexes upon the reaction entropy. Furthermore, we can study possible effects of the specific nature of the metal and of the electrode potential upon this parameter although such effects are not predicted by the Born model (vide infra).

Reaction Entropy. The parameter of interest, the reaction entropy, $\Delta S_{ex}°$, is contained in the Born–Haber cycle shown in Figure 1. Thus

$$\Delta S_{ex}° = [\Delta S_s°(z-1) - \Delta S_s°(z)] + [\Delta S_n°(z-1) - \Delta S_n°(z)] - \Delta S_v° \qquad (3)$$

Here, $\Delta S_s°(z)$ and $\Delta S_s°(z-1)$ are the electrostatic and $\Delta S_n(z)$ and $\Delta S_n(z-1)$ are the nonelectrostatic contributions to the single-ion entropy change that occurs when an ion A^z or A^{z-1} is introduced from vacuum into a solution. $\Delta S_{ex}°$ and $\Delta S_v°$ are the entropy changes due to the charge changes of A^z or A^{z-1} in solution and under vacuum, respectively.

The electrostatic entropy change for the electron-transfer process in vacuum is 0 (because $d\epsilon_0/dT = 0$). Only intramolecular contributions arising from the change in spin multiplicity and from changes in chemical bonds are present in $\Delta S_v°$. In the cases studied here (vide infra), only the spin contribution in $\Delta S_v°$ is left.

It is assumed and confirmed by empirical data[22] that $\Delta S_n°(z)$, which include also specific solvent–solute interactions, does not or nearly not depend on the charge. Thus, $\Delta S_n°(z) \approx \Delta S_n°(z-1)$, and while by definition $\Delta S_e° = \Delta S_s°(z-1) - \Delta S_s°(z)$, eq 3 reduces to eq 4. The experimental measured value needs only a correction for the change in spin multiplicity to obtain the pure electrostatic $\Delta S_e°$.

$$\Delta S_{ex}° = \Delta S_e° - \Delta S_v° \qquad (4)$$

Born Model. The simplest description of ionic solvation is given by the Born model, and it is easily shown[2] that for a one-electron reduction of a species with charge z the reaction entropy is given by eq 5, with the assumption that the radius

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(9) Abbreviations: R_2dtc^- = *N,N*-dialkyldithiocarbamate = $R_2NCS_2^-$; mnt = *cis*-1,2-dicyanoethenedithiolate = $(CN)_2C_2S_2^-$; R_2tu^- = *N*-phenyl-*N,N′*-dialkylthioureido = $R_2NC(S)NPh^-$; $pdtc^-$ = pyrrole-*N*-carbodithioate = $C_5H_5CS_2^-$; dtb = dithiobenzoate = $C_6H_5CS_2^-$; dtt = *p*-dithiotoluate = $CH_3C_6H_4CS_2^-$; dtn = dithionaphthoate = $C_{10}H_7CS_2^-$; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pent = pentyl; *i*-Bu = isobutyl; *i*-Pr = isopropyl; Pyr = pyrrolidyl; Pip = piperidyl; Mor = morpholyl; c-Hx = cyclohexyl; Bz = benzyl; Ph = phenyl.

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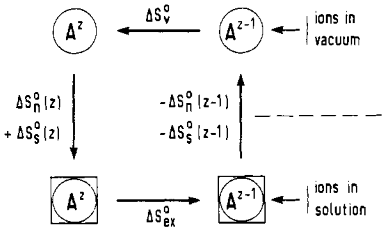

Figure 1. Born–Haber cycle for ionic solvation.

r is charge independent, which is true for at least the crystallographic radii (vide infra) of metal complexes.

$$\Delta S_{e,B}{}^{\circ} = \frac{N_a e^2}{\epsilon_s{}^2}\frac{d\epsilon_s}{dT}\frac{1-2z}{2r} \tag{5}$$

Although there is a temperature dependence for $\Delta S_{e,B}{}^{\circ}$ through the term $(1/\epsilon_s{}^2)d\epsilon_s/dT$, the variation of this term in the temperature range −20 to +30 °C is small for the solvent used (acetone; see also Table IV) and we assume $d(\Delta S_{e,B}{}^{\circ})/dT = 0$. So, $\Delta S_{e,B}{}^{\circ}$ is only dependent on the charge z and the radius r.[23] For transitions with opposite charges, the same values (apart from sign) for $\Delta S_{e,B}{}^{\circ}$ are obtained from a calculation with eq 5, as is intuitively expected for a structureless continuum. Thus, reduction of positively charged complexes is predicted to occur with an entropy gain ($\Delta S_e{}^{\circ} > 0$), and reduction of a neutral or a negatively charged complex should result in an entropy loss ($\Delta S_e{}^{\circ} < 0$).[24]

Furthermore, $\Delta S_{e,B}{}^{\circ}$ decreases when the radius of the ion increases because the electric field strength around an ion becomes smaller with increasing radius and so the ordering effect on the solvent dipoles is less important.

The Born equation usually give bad results for the ionic solvation entropy $\Delta S_s{}^{\circ}$ especially in aqueous media. However, the reaction entropy $\Delta S_{ex}{}^{\circ}$ is the difference of two $\Delta S_s{}^{\circ}$ values. So, the Born equation is now used in a rather relative way. Many of the possible objections against it are then avoided. Furthermore, the large size of the investigated complexes could result in a situation in which the Born equation is not much in error. Indeed, we showed elsewhere[4] that for the very voluminous ion $Au_9(PPh_3)_8{}^{3+}$ the Born prediction for the ratio of the two successive reductions of the cluster was very close to the experimental value. Anyhow, in this study trends are predicted well, and deviations lead to interesting conclusions.

In this paper we present a detailed study of the reaction entropy data of $M(dtc)_x{}^z$ complexes, and we will see that information concerning not only solvent reorganization but also charge distribution within the coordination compound itself can be obtained.

Experimental Section

General Procedures. The measurements have been carried out with a nonisothermal cell of the same design as that described by Weaver and co-workers.[1,2] The reaction entropy was calculated according to

$$\Delta S_{tot}{}^{\circ} = nF(dE_{1/2}/dT) \tag{6}$$

where n = 1− for an oxidation and n = 1+ for a reduction. Assuming $D_{ox} = D_{red}$, $E^{\circ} = E_{1/2}$. The half-wave potential was taken as the mean of the anodic and cathodic peak potentials in the cyclic voltammogram. The scan rate was chosen such that the anodic–cathodic peak potential difference was less then 100 mV for every transition and was usually 60–80 mV at 293 K. The *iR* drop was minimized by the use of a Luggin capillary. The typical temperature range used was −20 to +30 °C, except for Me_2SO where the temperature range was +14 to +43 °C. All potentials are referred to the Ag/AgCl (0.1 M LiCl, acetone) reference electrode. The working and auxiliary electrodes consisted of Pt.

Table I. Reaction Entropy Values of Pilot Experiments[a]

complex	$\Delta S_{ex}{}^{\circ}$, eu	remarks
$Fe(H_2O)_6{}^{3+/2+}$	38	reported value[b] 43
$Fe(bpy)_3{}^{3+/2+}$	4	reported value[b] 4
$Ni(mnt)_2{}^{2-/-}$	14.7	same values for oxidn
$Ni(mnt)_2{}^{-/2-}$	−14.1	and redn (apart from sign)
$Ni(mnt)_2{}^{2-/-}$	14.8	pretreated[c] electrode
$Ni(mnt)_2{}^{2-/-}$	14.7	not pretreated electrode
$Ni(mnt)_2{}^{2-/-}$	14.7	0.1 M Bu_4NClO_4
$Ni(mnt)_2{}^{2-/-}$	15.3	1.0 M Bu_4NClO_4
$Fe(Et_2dtc)_3{}^{0/+}$	−13.1	0.1 M Bu_4NClO_4
$Fe(Et_2dtc)_3{}^{0/+}$	−14.8	0.1 M $NaClO_4$

[a] First two entries measured in water, all others in acetone. [b] Reference 1. [c] Reference 33.

Equipment and Chemicals. The cyclic voltammograms were recorded with a Bioanalytical System CV-1B instrument or with a PAR 174A polarographic analyzer coupled with a PAR 175 programmer. Both instruments yielded identical results. Measurements were made in acetone (Merck p.a.), acetonitrile (Uvasol), or dimethyl sulfoxide (Merck p.a.). Because identical results for $\Delta S_{ex}{}^{\circ}$ were obtained for distilled and dried (molecular sieves, 3 Å) solvents as compared with untreated solvents, these solvents were used as received.

The supporting electrolyte, Bu_4NClO_4, was prepared as described,[22] recrystallized from an ethanol–ether mixture, and dried over P_2O_5. Measurements were made with 10^{-3} mol dm^{-3} complex solutions, and these were 0.1 mol dm^{-3} in supporting electrolyte. Metal dithiocarbamates,[6-8] $Cu(R_2tu)_2$,[28] $[Bu_4N]_2Ni(mnt)_2$,[29] $Ni(S_2C_2Ph_2)_2$,[29] $Fe(pdtc)_3$,[30,31] $Fe(dtb)_3$,[32] $M(dtt)_4$,[20] and $M(dtn)_4$[20] (M = Mo, W), were prepared as described in the literature. Satisfactory analytical (C, H, N) data were obtained for all compounds.

Pilot Experiments. To check the reliability of the equipment and of the measuring procedure, we carried out some pilot experiments, the results of which are given in Table I. For the oxidation of $Ni(mnt)_2{}^{2-}$ and the reduction of $Ni(mnt)_2{}^-$ nearly the same value was found, apart from sign. Pretreated[33] and not pretreated electrodes gave the same result, and for reproduced literature examples excellent agreement in results was obtained. Possible contributions to $\Delta S_{ex}{}^{\circ}$ from the Soret potential[34] arising from the temperature gradient between the working and the reference compartment are small and may be neglected as judged from the four last entries in Table I. Apparently the construction of the thermal liquid junction[1] yields enough convection to reduce the Soret effect to a neglectable amount.

The precision of the measurements is limited by the drift in the reference potential. This drift is in our setup, ca. 1–2 mV/50 K, which corresponds with 0.5–1 cal/mol K in $\Delta S_{ex}{}^{\circ}$.

The entries of Table I give detailed information about the reproducibility of the measurements. It can be estimated as 1 eu, which is comparable with that obtained by Weaver.

Weaver has discussed the reliability of the determination of $\Delta S_{ex}{}^{\circ}$ for the used setup, and we refer to that discussion.[1]

Results and Discussion

The entropy data for a set of transition-metal complexes

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Table II. Reaction Entropies ($\Delta S_{ex}°$ in eu) for Transition-Metal Complexes with Sulfur Donor Ligands in Acetone[a]

complex	redox couple 2+/1+	1+/0	0/1−	1−/2−
$Cu(Et_2dtc)_2$		22.5 (+0.67)	6.3 (−0.42)	
$Ni(Et_2dtc)_2$			5.3 (−1.40)	
$Pd(Et_2dtc)_2$			8.7 (−1.49)	
$Mn(Et_2dtc)_3$		11.7 (+0.38)	2.9 (−0.07)	
$Fe(Et_2dtc)_3$		13.1 (+0.51)	3.1 (−0.40)	
$Fe(Et_2dtc)_3$[b]		15.6	0.8	
$Co(Et_2dtc)_3$		11.6 (+1.30)		
$Mo(Et_2dtc)_4$	22.1 (+1.29)	13.4 (−0.23)		
$Mo(Et_2dtc)_4$[b]	24.1	15.9		
$W(Et_2dtc)_4$	21.6 (+0.92)	10.2 (−0.46)		
$Ni(S_2C_2Ph_2)_2$			−1.0 (+0.25)	−3.0 (−0.68)
$Ni(mnt)_2$				−12.9 (+0.40)
$Cu(Mortu)_2$		17.7 (+0.73)		
$Cu(Piptu)_2$		19.0 (+0.69)		
$Cu(ettu)_2$		21.6 (+0.65)		
$Fe(dtb)_3$			19.8 (−0.16)[c]	
$Fe(pdtc)_3$		19.7 (+1.27)	13.1 (+0.31)	
$Mo(dtt)_4$		13.0 (+0.78)		
$Mo(dtn)_4$		13.3 (+0.96)		
$W(dtt)_4$		9.7 (+0.76)		
$W(dtn)_4$		12.4 (+0.85)		

[a] Entropy values corrected for spin multiplicities $R \ln [(2S + 1)_{red}/(2S + 1)_{ox}]$. Half-wave potentials vs. Ag/AgCl reference electrode (0.1 M LiCl-acetone) in parentheses, in V. [b] Measured in 0.01 M instead of 0.1 M Bu_4NClO_4 (acetone). [c] Approximated value because the redox reaction is complicated by a chemical follow-up reaction at temperatures above 273 K.

Table III. Calculated[a] and Observed[b] Reaction Entropies (in eu) and Born (r_B) and Crystallographic (r_{cryst})[c] Radii for Groups of Metal Dithiocarbamates

complex	$\Delta S°$ (calcd) $z = z$	$z = z + 1$	$\Delta S_{ex}°$ (measd)	$\Delta(\Delta S_{ex}°)$	r_B, Å	r_{cryst}, Å
$M(Et_2dtc)_2^{+/0}$ (M = Cu)	7.9	23.6	22.5	15.9	3.7	4.6[d]
$M(Et_2dtc)_2^{0/-}$ (M = Cu, Ni, Pd)	−7.9	7.9	6.6			
$M(Et_2dtc)_3^{+/0}$ (M = Mn, Fe, Co)	4.5	13.6	12.1	9.1	6.4	5.1[e]
$M(Et_2dtc)_3^{0/-}$ (M = Mn, Fe)	−4.5	4.5	3.0			
$M(Et_2dtc)_4^{2+/+}$ (M = Mo, W)	15.0	25.0	21.9	10.1	5.8	5.8[f]
$M(Et_2dtc)_4^{+/0}$ (M = Mo, W)	5.0	15.0	11.8			

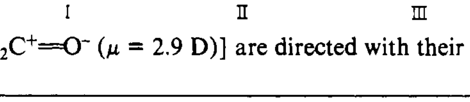
[a] Calculated with eq 5 and $r = r_B$. [b] Mean values for groups of bis-, tris-, and tetrakis(dithiocarbamates). [c] Calculated from $r_{cryst} = (3V/4\pi Z)^{1/3}$ where Z is the number of molecules per unit cell and V is the volume of the unit. [d] Bonamico, M.; Dessy, G.; Magnoli, A.; Variago, A.; Zambonelli, L. *Acta Crystallogr.* 1965, *19*, 886. Bonamico, M.; Dessy, G.; Mariani, C.; Variago, A.; Zambonelli, L. *Acta Crystallogr.* 1965, *19*, 619. Beurskens, P. T.; Cras, J. A.; Hummelink, Th. W.; Noordik, J. H. *J. Cryst. Mol. Struct.* 1971, *1*, 253. [e] Reference 15. Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1972, 1883. Leipoldt, J. G.; Coppens, P. *Inorg. Chem.* 1973, *12*, 2269. Merlino, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1968, *B24*, 1441. [f] van der Aalsvoort, J. G.; Beurskens, P. T. *Cryst. Struct. Commun.* 1974, *3*, 653. Wijnhoven, J. G. *Cryst. Struct. Commun.* 1973, *2*, 637.

with sulfur donor ligands are presented in Table II. For convenience all the redox transitions are written as reductions, although the transitions 2+/1+ and 1+/0 were actually measured as oxidations. These data are corrected for changes in spin multiplicities, $R \ln [(2S + 1)_{red}/(2S + 1)_{ox}]$. Only this correction is made while the inner entropy changes (e.g., the molecular vibrations or the $S_2C\overset{..}{-}N$ rotation) accompanying the transitions can be estimated to be less than about 1 eu.[35]

For all the transitions listed, $\Delta S_{ex}°$ decreases as the charge decreases. Further, as one proceeds from the $(dtc)_2$ to the $(dtc)_3$ complexes (i.e., as the radius increases), $\Delta S_{ex}°$ decreases. However, from the $(dtc)_3$ to the $(dtc)_4$ complexes, no clear-cut trend is present. So, it appears that the dependence of $\Delta S_{ex}°$ on z and r is at least qualitatively as predicted by eq 5.

In a quantitative way the experimental data disagree seriously with the outcome of the calculations from eq 5. The most noteworthy feature is that no change in sign occurs for $\Delta S_{ex}°$ from the 1+/0 to the 0/1− transition as is expected for reasons discussed in the Introduction. Furthermore, as can be seen in Table III, for the dithiocarbamates the observed $\Delta S°$ values are much better predicted by eq 5 when the charge is taken 1 unit larger than the real charge of the complex. This phenomenon may be caused by two (not quite independent) origins: the internal charge distribution of the metal complex and the asymmetry of the solvent dipoles.

Internal Charge Distribution within the dtc Complexes. It is well-known that in the metal–dtc complexes the ionic charge of the metal is nearly completely compensated by the covalency in the bonding of the ligand, which causes a flow of π electrons from the nitrogen atom to the metal center. Keijzers[36] calculated for the atomic charges of copper and sulfur in $Cu(R_2dtc)_2$ the very small values of 0.04 and −0.28, respectively. As a consequence, the atomic charge of the nitrogen will be positive. Moreover even in the case when the total charge of the complex is negative, the nitrogen remains positively charged. Indeed the infrared stretching frequencies of the $S_2C–N$ bond of some negatively charged $M(R_2dtc)_x$ complexes[37,38] suggest a significant contribution of resonance structure III to the overall structure. So, the acetone dipoles



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$[(CH_3)_2C^+\!=\!O^-$ (μ = 2.9 D)] are directed with their negative

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ends toward the more positively charged nitrogen atoms. Support for such interactions can be gained by considering the positions of the negative ions in the crystals of cationic metal dithiocarbamates like $[Cu(R_2dtc)_2]I_3$,[39] $[Au(R_2dtc)_2]X$ (X = Br,[40] $AuCl_2$,[41] $AuBr_2$[41]), and $[Ni(R_2dtc)_3]Br$,[42] where the anions are located in the pockets formed by the alkyl chains, i.e. in direct contact with the nitrogen atoms. So, it is expected that in solution the nitrogen atoms will be solvated more effectively than the other atoms in the molecule. For the bis complexes this stereochemical argument seems not appropriate since the square four-coordination leaves the metal exposed to the solvent.

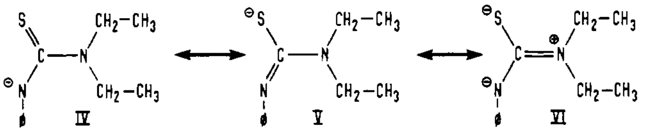
The Born model (eq 5) assumes the solvated ion to be a point charge. Taking the formal charge z as the effective charge is only permitted for solvent–solute interactions at infinite distance. At finite distance one has to incorporate the charge distribution within the ion. For a species with multiple-charge centers with effective radii (r_i), the Born formula has to be modified to

$$\Delta S_{\mathrm{mc,B}} = (N_a e^2/\epsilon_s^2)(\mathrm{d}\epsilon_s/\mathrm{d}T)\sum_i[(\Delta n_i^2 - 2z_i(\Delta n_i))/2r_i] \qquad (7)$$

when charge changes Δn_i occur upon reduction. Note that z_i need not to be an integral and that the sign of the summing term in this equation can be opposite to that of $(1 - 2z)/2r$ in eq 5. This modification resembles the refinement that Peover[43] made for the expression of the Marcus free energy of activation for molcules with a nonuniform charge distribution. Because the values of Δn_i are not known, a numerical calculation of $\Delta S_{\mathrm{mc,B}}$ cannot be performed. The experimental data indicate that even for negatively charged complexes the electrostatic interactions of the partial positively charged nitrogen atoms prevail and the complexes actually behave like a cation. As shown in Table III much better agreement between $\Delta S_{ex}°$ and the calculated values is obtained by inserting in eq 5 the (arbitrarily) effective charge $z + 1$ instead of the formal charge z of the complex.

To demonstrate the characteristic influence of electronic and structural features of ligands, a limited number of entropy data for other metal complexes containing sulfur donor ligands are also presented in Table II.

The thiourea (tu) derivatives (structures IV–VI) are isoelectronic with the dtc ligand. The metal complexes have in common a high C–N bond order and consequently a restricted rotation around C–N, and a considerable positive charge on the nitrogen. The $E°$ and $\Delta S_{ex}°$ values of the copper complexes are very close to those of the copper dithiocarbamates.



IV V VI

The ligands $Ph_2C_2S_2^{2-}$ and mnt^{2-} are structurally very different as compared with the dtc ligand. No positive charge can be transferred to the peripheri of the metal complexes derived therefrom. In contrast with $Ni(Et_2dtc)_2$, negative $\Delta S_{ex}°$ values are observed for the 0/1– and 1–/2– reductions of the nickel complexes.

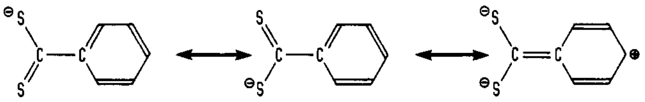
Table IV. Influence of the Solvent upon $\Delta S_{ex}°$ for $M(Et_2dtc)_x^z$ Reductions[a] and Physical Constants[b] for the Solvents Used

constant	acetone	acetonitrile	Me_2SO
dielectric const, ϵ_s	20.5	36.0	46.7
$\mathrm{d}\epsilon_s/\mathrm{d}T$	−0.09	−0.16	−0.106
$10^4(1/\epsilon_s^2)(\mathrm{d}\epsilon_s/\mathrm{d}T$	−2.14	−1.23	−0.49
a, cal mol^{-1} K^{-1}	−27.6	−18.3	−9.9

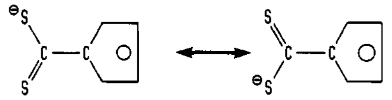
	$\Delta S_{ex}°$, eu		
complex	acetone	acetonitrile	Me_2SO
$Cu(Et_2dtc)_2^+$	22.5	16.9 (5.1)	15.8[c] (2.0)
$Cu(Et_2dtc)_2$	6.3	−3.4 (−5.1)	5.1 (−2.0)
$Fe(Et_2dtc)_3^+$	13.1	7.5 (2.9)	7.7 (1.1)
$Fe(Et_2dtc)_3$	3.1	−4.0 (−2.9)	d
$W(Et_2dtc)_4^{2+}$	21.6	15.9 (9.6)	
$W(Et_2dtc)_4^+$	10.2	2.6 (3.2)	

[a] Values for $\Delta S°$ calculated with eq 5 are given in parentheses. For calculated values in acetone, see Table III. [b] Physical constants from: Abraham, M. H.; Liszi, J. *J. Chem. Soc., Faraday Trans. 1* 1978, *74*, 2858. [c] Complicated by a chemical reaction at temperatures above 35 °C. [d] Irreversibility precludes determination of $\Delta S_{ex}°$.

pdtc,[30,31] dtb,[32] dtt,[20] and dtn[20] ligands have in common little conjugation of the CS_2 group with the aromatic rings in their metal complexes. (structures VII–XI). This causes a free rotation of the rings around the $S_2C–C$ bond (i.e., structures like IX and XI are of no importance) and a localization of charge changes in the metal–sulfur–carbon core. This in contrast with the dtc complexes. $\Delta S_{ex}°$ values for the Fe complexes of pdtc and dtb differ much from those of the corresponding dtc complexes in that these values are higher (13.1 together with 19.8 eu compared with 3.1 and 19.7 compared with 13.1 eu), which is unexpected and up to now not well understood. For the Mo and W complexes the $\Delta S_{ex}°$ values are about the same as for the analogous dtc complexes. Although some speculative explanations are possible, we refrain here from further discussion.



VII VIII IX



X XI

Stereochemistry of the Solvent Dipole. The charge distribution in the acetone dipole (possible refinements such as quadrupoles will be disregarded) is asymmetric such that the steric environment of the atom carrying the positive charge is different from the environment of the atom carrying the negative charge. There will be no doubt that the acetone layer surrounding a cation will be more structured than the layer surrounding an anion, since the positive site of the acetone dipole is much more shielded than the negative site[44] [$(CH_3)_2C^+{=}O^-$ (μ = 2.9 D)]. The uncharged dtc complexes provoke an ordering of the surrounding solvent, which can be more ordered than for the 1– charged complex, because of the particular charge distribution as described above. So it can be understood that on going from the uncharged to the negatively charged complex there is loss in local solvent order,

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(44) In aqueous solution a similar difference between positive and negative ions is observed as the heat of hydration of positive ions is definitely higher than that of the negative ions of the same size and charge. Bockris, J. O.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1970; Vol. 1, p 68.

Table V. Substituent Effect upon ΔS_{ex}° [a,b] for the Reduction of $M(R_2dtc)_x^z$ in Acetone

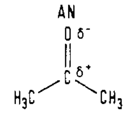
	substituent R[c]									
	Bz	Pyr	Et	Pr	Bu	Pent	Pip	*i*-Bu	*i*-Pr	c-Hx
$Ni(R_2dtc)_2$	8.6		5.3	5.7	7.4	10.0	7.5	8.6	6.8	
$Cu(R_2dtc)_2$			6.3	6.7	10.5	9.0	6.3	10.7	5.9	
$Fe(R_2dtc)_3$	7.8	4.0	3.1	3.9	4.6	3.5		5.5		
$Mn(R_2dtc)_3$	4.1		2.9							5.5
$Cu(R_2dtc)_2^+$			22.5	22.8	24.0	22.9	24.0	23.8	21.8	
$Co(R_2dtc)_3^+$	8.2		11.6	8.5	8.3	8.9		11.7	7.6	8.3
$Fe(R_2dtc)_3^+$	11.9	13.3	13.1	13.7	12.4	12.4		14.8	11.0	10.9
$Mn(R_2dtc)_3^+$	17.2		11.7				16.8			12.5

[a] In cal/mol K. [b] Corrected for change in spin multiplicity. [c] From left to right, R substituent shows increasing electron-donating properties.

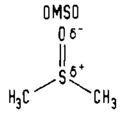
i.e. the minimum of solvent order does not coincide with the neutral state of the complex.

To study this effect we determined the ΔS_{ex}° for a few selected redox couples in acetonitrile and dimethyl sulfoxide (Me_2SO). The results are collected in Table IV. Before interpreting these data one should be aware that in changing of the solvent at least the following features are changed: (i) The steric shielding of the solvent dipoles as discussed above is altered. (ii) The dielectric constant and its temperature coefficient are changed. For this reason it is expected that $|\Delta S_{ex}^{\circ}|$ will decrease in the sequence acetone > acetonitrile > Me_2SO.[2,45] (iii) The degree of internal order (a) has been shown to be in the order Me_2SO > acetonitrile > acetone. When the internal order is low (a more negative) the additional ordering of the solvent molecules will be stronger when the charge of the ion increases. So, we expect that $|\Delta S_{ex}^{\circ}|$ will decrease in the sequence acetone > acetonitrile > Me_2SO (Table IV). This is the same sequence as found under (ii).

From the molecular solvent structures (XII–XIV) it is clear



XII



XIII

XIV

that the steric shielding of the positive side of the dipole is much less in acetonitrile as compared with acetone and Me_2SO, where the steric shielding is virtually the same. Therefore, it is expected that ΔS_{ex}° values measured in acetonitrile are much better predicted by calculated values from eq 5. Indeed, the data of Table IV show the expected change of sign for the 0/1− transitions in contrast with the values obtained for acetone and Me_2SO. When acetonitrile and Me_2SO are compared, the orders predicted under (ii) and (iii) are (partly) counteracted by the effect from (i). Indeed, the $|\Delta S_{ex}^{\circ}|$ values for Me_2SO are not definitely lower than those obtained in acetonitrile as would have been expected on account of only the reasons under (ii) and (iii). However, when comparing acetone and Me_2SO, we have only to consider the effects under (ii) and (iii) because of the similar dipole structures of these solvents. The trend in ΔS_{ex}° is now indeed as predicted under (ii) and (iii): ΔS_{ex}°(acetone) > ΔS_{ex}°(Me_2SO).

Influence of the Size of the Complexes. Equation 3 predicts a decrease in ΔS_{ex}° with increasing radius, and this was seen indeed on going from the $(dtc)_2$ to the $(dtc)_3$ complexes.

For a two-step electron-transfer series like

$$M(Et_2dtc)_x^{z} \xrightarrow{\Delta S_1^{\circ}} M(Et_2dtc)_x^{z-1} \xrightarrow{\Delta S_2^{\circ}} M(Et_2dtc)_x^{z-2} \quad (8)$$

the difference in reaction entropies for the two steps is given by

$$\Delta(\Delta S^{\circ}) = \Delta S_2^{\circ} - \Delta S_1^{\circ} \quad (9)$$

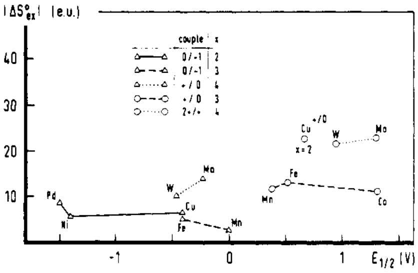


Figure 2. Influence of the half-wave potential ($E_{1/2}$) upon the reaction entropy (ΔS_{ex}°) for $M(Et_2dtc)_x^z$ complexes.

After substitution of eq 5 and insertion of the correct constants ($d\epsilon_s/dT = -0.09$, $\epsilon_s = 20.45$ for acetone)

$$\Delta(\Delta S^{\circ}) = -58.1/r_B \quad (10)$$

with $\Delta(\Delta S^{\circ})$ in eu and r_B in Å. It is assumed that the radii are independent of the charge of the complex as suggested by many crystallographic radii.[46] The advantage of the expression (10) is that the knowledge of the effective charge distribution of the complex is not needed. Because the majority of crystallographic data are known for the diethyl-substituted complexes, the following discussion is limited to dtc complexes with this substituent. The complexes are classified into three groups, and the results are presented in Table III. Crystallographic radii (r_{cryst}) were calculated from crystallographic data approximating the molecules as spheres.

There is a resonable agreement between the Born radii and the crystallographic radii. That $r_B < r_{cryst}$ for the bis complexes is understandable because the flatness of the complex allows solvent molecules a close approach, and treating the complex as a sphere is a very crude approximation. We expect r_B(bis) > r_B(tris) because of the crystallographic radii; however, it is not clear why r_B(tetrakis) < r_B(tris). The agreement between r_B and r_{cryst} for the tetrakis complexes is excellent. This might be due to the fact that the approximation of the molecules by a sphere is most accurate for the tetrakis complexes.

Influence of the Specific Nature of the Metal. Inspecting Tables II and V for a possible influence of the metal shows that after the correction for the change in spin multiplicity there remains only small differences without clear trends. This lack of a metal influence has been found earlier for a variety of aqua, amine, and N-chelated ligand complexes[2] and is in accord with theoretical expectations. It justifies division into groups as done in the preceding discussion.

Influence of Half-Wave Potential and Substituent R. Since the half-wave potentials of the electron-transfer reactions studied here vary considerably (from −1.4 to +1.3 V), it is of interest to search for a possible correlation of ΔS_{ex}° with the

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[45] Criss, C. M. *J. Phys. Chem.* **1974**, *78*, 1000.

[46] For $Fe(Pyrdtc)_3$ (r = 5.24 Å) and $Fe(Pyrdtc)_3^+$ (r = 5.25 Å) the same radii were found.[15,47]

[47] Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1163.

half-wave potential as suggested by

$$E_{1/2} = -\Delta G°/F = -\Delta H°/F + T\Delta S°/F \qquad (11)$$

The data are collected in Figure 2; complexes with the same coordination class and the same charge are connected with lines. It is obvious from the figure that there is no correlation between $\Delta S_{ex}°$ and $E_{1/2}$. Thus, we conclude that the differences in $\Delta H°$ dominates the much smaller differences in $T\Delta S_{tot}°$. This is an important conclusion from the experimental data. It has often been assumed tacitly for dtc and other complexes in numerous studies about the relation between redox potentials and binding energies, ionization energies, and ligand field parameters.[48]

The differences in redox potential discussed so far are due to the specific nature of the central metal. Martin et al.[19] showed that on changing the substituent R the half-wave potential could be varied over 200–300 mV for each metal. In order to investigate whether this variation in redox potential is of enthalpic, entropic, or a mixed character we measured $\Delta S_{ex}°$ for transitions of dtc complexes with varying R. The results are presented in Table V.

The R substituents are arranged in such a way that the redox potential increases on going from the left to the right. Despite the well-defined influence of the R substituents upon $E_{1/2}$ and apart from some exceptional values (i.e., the reduction of $Mn(Bz_2dtc)_3^+$ and $Mn(Pipdtc)_3^+$), a clear trend is not present. The spreading in the data is largest for the bis complexes for the 0/1– transitions. As long as R = alkyl there is a small variation in $\Delta S_{ex}°$, but for the $Cu(R_2dtc)_2^{+/0}$ couples, $\Delta S_{ex}°$ is almost independent of R. This is consistent with the fact that the entropies of solution for flexible alkanes are all the same.[49] Apart from this, the influence of R can be very complicated as it will be a function of at least (i) the electron-donating and -withdrawing power of the substituent, (ii) the steric hindrance of the two groups, and (iii) the influence on the "effective" radius of the molecule and possible specific solvent interaction.

Ion-Pair Effects. The question arises whether the trends fround could be due to ion–ion interactions between the complex ions and the ions of the supporting electrolyte.

Ion-pair forming should be accompanied with an entropy gain ($\Delta S_{ex}° > 0$) for the 1+/0 transitions and an entropy loss ($\Delta S_{ex}° < 0$) for the 0/1– transitions. This is the same trend as predicted from the simple solvation models (see above). Furthermore, it can be argued from the geometry of the Bu_4N^+ and ClO_4^- that ClO_4^- can solvate cations more effectively than Bu_4N^+ can solvate anions. This is the same as what is expected from the solvents used here: cations will be more effectively solvated than anions. However, in the sequence acetone to acetonitrile to Me_2SO, the ion-pair formation is expected to become less important because the dielectric constant increases in this order. This is in contrast with the outcome of the experiments (Table IV): the $\Delta S_{ex}°$ results for Me_2SO and acetone are comparable and not symmetric for 1+/0 and 0/–1 transitions whereas acetonitrile (intermediate ϵ_s) behaves much more according to a "symmetric dipole".

More information to clarify the point can be gained from the data of $Fe(Et_2dtc)_3$ and $Mo(Et_2dtc)_4$ measured in solutions that were 0.01 M instead of 0.1 M in supporting electrolyte (Table II), from the data of $Ni(mnt)_2^{2-/-}$ measured in 0.1 M and 1.0 M Bu_4NClO_4 (Table I), and from data of $Fe(Et_2dtc)_3^{0/+}$ measured in 0.1 M Bu_4NClO_4 and 0.1 M $NaClO_4$ (Table I). The differences in $\Delta S_{ex}°$ obtained in these media are not more than only 2.5 cal/mol K.

So, ion-pair effects give only small contributions to $\Delta S_{ex}°$ in this study. Although ion pairs are certainly present, they do not mask the specific contributions of the solvent dipoles and the geometry and charge distributions of the complex ions.

Conclusions

This study shows that $\Delta S_{ex}°$ values can give interesting information about transition-metal complexes and their surroundings in solution. The general trends in the experimental data clearly indicate that both the charge distributions in the complex and the symmetry of the solvent dipole play a role in the ultimate value of $\Delta S_{ev}°$.

The expression for $\Delta(\Delta S_{ex}°)$, derived with the Born model, yields a surprisingly good agreement between the Born radii and the crystallographic radii. The well-established influence of the metal and of the substituent R upon the half-wave potentials $E_{1/2}$ of transition-metal dithiocarbamates is not reflected in the $\Delta S_{ex}°$ values. It is now experimentally verified that the intuitive interpretation of $E_{1/2}$ values as enthalpic values is allowed since the variation in $\Delta S_{ex}°$ values can account for only a very small part in the variation of $E_{1/2}$ values, of course within one coordination class and for couples with the same charge.

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Registry No. $Cu(Et_2dtc)_2$, 13681-87-3; $Ni(Et_2dtc)_2$, 52610-81-8; $Pd(Et_2dtc)_2$, 15170-78-2; $Mn(Et_2dtc)_3$, 15740-71-3; $Fe(Et_2dtc)_3$, 13963-59-2; $Co(Et_2dtc)_3$, 13963-60-5; $Mo(Et_2dtc)_4$, 41947-30-2; $W(Et_2dtc)_4$, 12571-26-5; $Ni(S_2C_2Ph_2)_2$, 28984-20-5; $Ni(mnt)_2$, 19280-13-8; $Cu(Mortu)_2$, 78363-42-5; $Cu(Piptu)_2$, 78363-44-7; $Cu(ettu)_2$, 78363-39-0; $Fe(dtb)_3$, 26149-31-5; $Fe(pdtc)_3$, 21288-86-8; $Mo(dtt)_4$, 61160-42-7; $Mo(dtn)_4$, 61160-43-8; $W(dtt)_4$, 61160-44-9; $W(dtn)_4$, 61160-45-0; $Ni(Bz_2dtc)_2$, 38542-61-9; $Ni(Pr_2dtc)_2$, 14516-30-4; $Ni(Bu_2dtc)_2$, 13927-77-0; $Ni(Pent_2dtc)_2$, 36259-37-7; $Ni(Pip_2dtc)_2$, 41476-75-9; $Ni(i\text{-}Bu_2dtc)_2$, 28371-07-5; $Ni(i\text{-}Pr_2dtc)_2$, 15694-55-0; $Cu(Pr_2dtc)_2$, 14354-08-6; $Cu(Bu_2dtc)_2$, 52691-95-9; $Cu(Pent_2dtc)_2$, 36190-66-6; $Cu(Pip_2dtc)_2$, 15225-85-1; $Cu(i\text{-}Bu_2dtc)_2$, 51205-55-1; $Cu(i\text{-}Pr_2dtc)_2$, 14354-07-5; $Fe(Bz_2dtc)_3$, 23451-11-8; $Fe(Pyr_2dtc)_3$, 21288-86-8; $Fe(Pr_2dtc)_3$, 15407-44-0; $Fe(Bu_2dtc)_3$, 14526-32-0; $Fe(Pent_2dtc)_3$, 23674-37-5; $Fe(i\text{-}Bu_2dtc)_3$, 19543-96-5; $Mn(Bz_2dtc)_3$, 33291-11-1; $Mn(c\text{-}Hx_2dtc)_3$, 27796-39-0; $Cu(Et_2dtc)_2^+$, 46763-10-4; $Cu(Pr_2dtc)_2^+$, 59093-12-8; $Cu(Bu_2dtc)_2^+$, 51018-22-5; $Cu(Pent_2dtc)_2^+$, 91670-35-8; $Cu(Pip_2dtc)_2^+$, 91670-36-9; $Cu(i\text{-}Bu_2dtc)_2^+$, 91670-37-0; $Cu(i\text{-}Pr_2dtc)_2^+$, 59765-88-7; $Co(Bz_2dtc)_3^+$, 91670-38-1; $Co(Et_2dtc)_3^+$, 52637-77-1; $Co(Pr_2dtc)_3^+$, 91670-39-2; $Co(Bu_2dtc)_3^+$, 55060-07-6; $Co(Pent_2dtc)_3^+$, 91670-40-5; $Co(i\text{-}Bu_2dtc)_3^+$, 91686-37-2; $Co(i\text{-}Pr_2dtc)_3^+$, 52637-79-3; $Co(c\text{-}Hx_2dtc)_3^+$, 52637-81-7; $Fe(Bz_2dtc)_3^+$, 49857-66-1; $Fe(Pyr_2dtc)_3^+$, 47384-11-2; $Fe(Et_2dtc)_3^+$, 47383-99-3; $Fe(Pr_2dtc)_3^+$, 65643-05-2; $Fe(Bu_2dtc)_3^+$, 55060-16-7; $Fe(Pent_2dtc)_3^+$, 91670-41-6; $Fe(i\text{-}Bu_2dtc)_3^+$, 65643-04-1; $Fe(i\text{-}Pr_2dtc)_3^+$, 47670-51-9; $Fe(c\text{-}Hx_2dtc)_3^+$, 47874-02-2; $Mn(Bz_2dtc)_3^+$, 91670-42-7; $Mn(Et_2dtc)_3^+$, 52699-11-3; $Mn(Pip_2dtc)_3^+$, 53738-04-8; $Mn(c\text{-}Hx_2dtc)_3^+$, 83201-89-2.

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