higher than the factor obtained with EDTA. This behavior could be utilized in preparing pure yttrium from naturally occurring mixtures, where the main impurity is generaly dysprosium. A two-step ion-exchange process using first BEDTA to eliminate the Dy and then hot EDTA to eliminate the Tb would offer a definite advantage over separations using only EDTA. An improvement in both separation time and purity could be expected. Ion-exchange schemes using cold HEDTA to separate yttrium from the heavier lanthanides have not proven successful.

Finally, the water solubility of BEDTA is around 7 g/L, lower than that of either MEDTA or HEDTA but markedly higher than the solubility of EDTA. Therefore H^+ can be used as the retaining ion in systems employing BEDTA as the eluent. In addition to the lower costs and easy recycle associated with the H^+ retaining ion, the resultant faster kinetics at the front of the band would be advantageous.

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Registry No. BEDTA, 65311-06-0; *N*-benzylethylenediamine, 4152-09-4; formaldehyde, 50-00-0; NaCN, 143-33-9; La(BEDTA), 65338-61-6; Ce(BEDTA), 65338-60-5; Pr(BEDTA), 65338-59-2; Nd(BEDTA), 65338-58-1; Sm(BEDTA), 65338-57-0; Eu(BEDTA), 65338-56-9; Gd(BEDTA), 65338-70-7; Y(BEDTA), 65366-45-2; Tb(BEDTA), 65338-69-4; Dy(BEDTA), 65338-68-3; Ho(BEDTA), 65338-67-2; Er(BEDTA), 65338-66-1; Tm(BEDTA), 65452-42-8; Yb(BEDTA), 65338-65-0; Lu(BEDTA), 65338-64-9.

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Nitrogen Nuclear Magnetic Resonance Spectroscopy. 10. *N*-Sulfinylamines and *N*-Sulfenamides

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We report ^{14}N shifts, measured by wide-line methods, which help to establish characteristic regions for sulfur–nitrogen groupings. In the sulfenamides $R_2N{-}SAr$ the lines are at high field in what may be termed the S–N single-bond region, since the resonances of (cyclic) *N*-methylsulfurimides[1] are nearby, as are those of the singly bonded nitrogen in $R_2\mathit{N}SNSO$ (Table I).

Sulfinylamines $XN{=}S{=}O$ were formerly thought to be analogues of thiocyanates $XN{=}C{=}S$; however, imido nitrogen in linear systems with cumulated double bonds (such as thiocyanate XNCS,[2a] cyanate XNCO,[2b] carbodiimide $RN{=}C{=}NR$,[2c] and azide $X\mathit{N}NN$[2d]) resonates at fairly high field. The –NSO region is some 200–300 ppm downfield of this, at medium field, as for $XN{=}Y$ and conjugated groupings, examples of which are sulfimide $-N{=}S{=}N-$ as in S_4N_2[1] and other cyclothiazenes[3,4] and azines such as pyridine or pyrimidine.[5] In accordance with this the XNSO grouping is cis-bent in the molecules that have been measured (MeNSO,[6] H_3SiNSO,[7] $S(NSO)_2$,[8] ClNSO,[9] and HNSO[10]) with bond angles of about 120° at nitrogen and sulfur.

Table I. Nitrogen Chemical Shifts in *N*-Sulfinylamines, *N*-Sulfenamides, and Related Compounds

Compd[a]	$\delta(NH_4^+)$/ ppm[b]	*w*/ Hz[c]	*tw*/ Hz[d]	S:N	Ref (NMR)	λ_{max}/ nm[e]	log ϵ[f]	Ref (UV)
1,4-$S_6(NMe)_2$ (CS_2)	−2 (5)				1			
S_7NMe (CS_2)	−2 (5)				1			
Me_2NSPh	4 (10)	700		3.5:1				
Et_2NSPh	9	720		1.3:1				
$Me_2\mathit{N}SNSO$	18 (5)		450					
n-$Pr_2\mathit{N}SNSO$	30 (10)	900		1.3:1				
FSO_2NSO	274	225		75:1				
$S(NSO)_2$ (100 °C)	282					377	4.0	*g*
PhNSO	294					315	4.0	*h*
PhSNSO	296 (4)	600		40:1				
n-$Pr_2NS\mathit{N}SO$	303	730						
Me_3SiNSO	309		47			283[i]	1.5[i]	7[i]
$Me_2NS\mathit{N}SO$	322 (2)		210					
Me_3CNSO	332 (2)		76	10:1		305	1.6	16
CF_3SNO (−80 °C)	695			10:1	12	570	0.8	12
EtSNO	765			7:1	12	550	1.3	12

[a] Measured as neat liquids at room temperature unless a solvent or temperature is given. [b] Relative to NH_4^+(aq), positive downfield. The precision depends on the line width (figures in parentheses are the estimated probable errors in the last digit, usually better than ±5 ppm). [c] Peak-to-peak width (±5–10%) of the derivative line, with modulation at 20–40 Hz. The lines are modulation broadened, particularly at low S:N ratios. [d] Line width at half-height, measured by the side-band method, with modulation at 500 Hz. [e] Wavelength of longest wavelength band. [f] The units of ϵ are L mol^{-1} cm^{-1}. [g] M. Becke-Goehring and J. Heinke, *Z. Anorg. Allg. Chem.*, 272, 297 (1953). [h] G. Kresze and H. Smalla, *Ber. Dtsch. Chem. Ges.*, 92, 1042 (1959). [i] These values are for H_3SiNSO.

An inverse dependence of the paramagnetic term on the energy of the $n_N \rightarrow \pi^*$ circulation in $XN{=}Y$ compounds has been observed.[11,12] We find that the XNSO region follows in the sequence[11] in which the nitrogen line goes downfield (and the $n_N \rightarrow \pi^*$ band to longer wavelengths) as the electronegativity of the atom Y doubly bonded to nitrogen decreases; that is, δ and λ increase in order $XN{=}S{=}O \sim XN{=}CR_2 < XN{=}NX < XNO$. Thus the *N*-sulfinylamines resonate in the same region as the azomethines $RN{=}CR_2$. The –NSO group is colorless; for the isomeric thionitrosyl compounds $XSN{=}O$, which are red, the nitrogen resonance appears 400 ppm to lower field, and the blue *C*-nitroso compounds resonate at lower field still (Table I).[11,12]

Within the XNSO series, however, δ does not correlate with the longest wavelength band (Table I) because this represents excitation from sulfur not nitrogen. These compounds are imido derivatives of SO_2, for which the $n_S \rightarrow \pi^*$ singlet absorption is at 290 nm;[13] cf. 210 nm for R_2SO.[14] The $n_N \rightarrow \pi^*$ absorption is expected to be at shorter wavelengths and has not as yet been characterized.

Among the XNSO compounds the resonance at highest field is that of FSO_2NSO, in which the electronegative X group stabilizes the σ relative to the π^* MO's. If allowance is made for the diamagnetic effect of heavy-atom ligands (Si, S) on

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the nitrogen, then the paramagnetic term is relatively large for –NSO with these ligands, which implies a lowering of the π^* relative to the n_N orbital.

Nitrogen-14 shifts were measured as before.[11] Literature methods were used for the preparation of $S(NSO)_2$,[15] PhNSO,[16] R_2NSAr,[17] and R_2NSNSO.[18]

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Registry No. Me_2NSPh, 24380-79-8; Et_2NSPh, 6667-19-2; Me_2NSNSO, 53520-63-1; *n*-Pr_2NSNSO, 65036-40-0; FSO_2NSO, 16829-30-4; $S(NSO)_2$, 13840-74-9; PhNSO, 1122-83-4; PhSNSO, 28968-93-6; Me_3SiNSO, 7522-26-1; Me_3CNSO, 38662-39-4.

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Photoinduced Dissociation of Oligomeric Tetrakis(methyl isocyanide)iridium(I)

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Bedford and Rouschias have briefly reported the photochemical properties of $[Ir(CNCH_3)_4]^+$.[1] The chloride salt of the complex was described as a blue-black air-sensitive solid which gave deep blue solutions (λ_{max} 610 nm; ϵ 22 000) in the absence of oxygen. These solutions were stable for several days in the dark, but they rapidly turned red-orange within minutes in light. On the basis of slight shifts in the NMR spectrum during photolysis and the somewhat reversible nature of the reaction, it was suggested that photoinduced association of solvent occurred to give a stable solvated complex, eq 1.[1] In

$$[\mathrm{Ir(CNCH_3)_4}]^+ + \mathrm{S} \overset{h\nu}{\rightleftarrows} [\mathrm{Ir(CNCH_3)_4(S)}]^+ \qquad (1)$$

$$\mathrm{S} = \mathrm{(CH_3)_2CO, CH_3CN, CH_3OH}$$

support of this proposal, it was shown that whereas aqueous solutions of $[Ir(CNCH_3)_4]^+$ did not react with CO or excess $CNCH_3$ in the dark, they did so when irradiated to give the corresponding $[Ir(CNCH_3)_5]^+$ and $[Ir(CNCH_3)_4CO]^+$ adducts.[1]

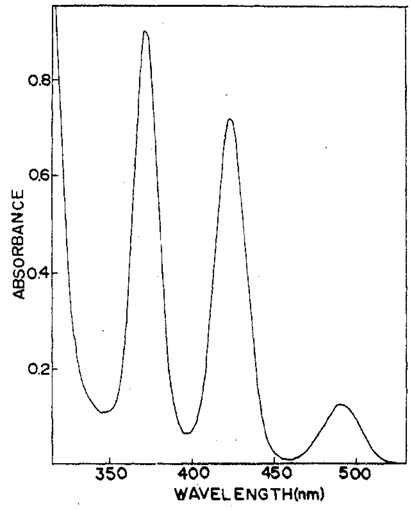

Figure 1. Electronic absorption spectrum of $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$ in CH_2Cl_2 solution.

It is our intent in this note to demonstrate that $[Ir(CNCH_3)_4]^+$ does not exist as a monomeric complex in solution but rather as oligomeric $[Ir(CNCH_3)_4]_n^{n+}$. We further show that the photochemical reaction is not photoinduced association as previously suggested[1] but rather photoinduced dissociation of the solution oligomers to generate monomeric $[Ir(CNCH_3)_4]^+$.[2,5] It is then monomeric $[Ir(CNCH_3)_4]^+$ which subsequently undergoes addition of $CNCH_3$ or CO.

Results and Discussion

$[Ir(CNCH_3)_4]Cl$ can be prepared as previously described[1] by the addition of $CNCH_3$ to *trans*-$[IrCl(CO)(PPh_3)_2]$. We have found a more convenient preparation to be through the addition of excess $CNCH_3$ to $[IrCl(1,5\text{-cyclooctadiene})]_2$. The blue-black solid obtained from this reaction is soluble in MeOH and H_2O and gives dark blue or blue-violet solutions. In addition to the dark solid, an amorphous, highly reflecting gold-colored material was obtained by very slow evaporation of solvent from methanol solutions. Dissolution of the gold-colored material gave the characteristic dark blue solutions which again yielded the blue-black powder upon rapid evaporation of solvent.

Preparation of $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$ by an exactly analogous procedure using excess *tert*-butyl isocyanide gave an orange solid in contrast to the dark material obtained with $CNCH_3$. Its infrared spectrum showed a single $\nu_{C\equiv N}$ at 2160 cm^{-1} similar to that of $[Ir(CN\text{-}t\text{-}Bu)_4]PF_6$ previously prepared by a somewhat different procedure.[4] The electronic absorption spectrum of $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$ in CH_2Cl_2 solution, Figure 1, shows bands at 490 (ϵ 743), 423 (ϵ 4264), 372 (ϵ 5428), and 309 nm (ϵ 16 787). It is precisely the type of spectrum shown by the other planar Ir(I) complexes which we previously examined,[8-10] and it is virtually identical with the spectrum of $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$. Thus $[Ir(CN\text{-}t\text{-}Bu)_4]^+$ behaves exactly as expected for a monomeric Ir^IL_4 complex.

The electronic absorption spectrum of a dark blue methanol solution of $[Ir(CNCH_3)_4]Cl$ is shown in Figure 2. It is not at all similar to the spectrum of $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$ or to the spectra of other planar Ir(I) complexes[8-10] but instead shows a maximum at 630 nm with an apparent ϵ of 16 000, calculated for a solution 1.77×10^{-3} M in monomeric $[Ir(CNCH_3)_4]Cl$. The band maximum varies between 600 and 650 nm, depending on concentration and the method of sample preparation. The intensity of the 630-nm band does not follow