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Diamagnetic Susceptibilities of Some Cyclic Dialkylsilylamidoximes

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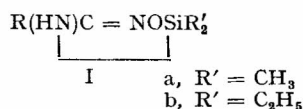
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The diamagnetic susceptibilities of some newly synthesized dialkylsilylamidoximes derived from dialkyl-dichlorosilanes and amidoximes have been determined and found to be in good agreement with calculated values obtained by the method of Baudot. The χ_{Si} and χ_{CH_2} values have also been reported and the lower values of χ_{Si} have been explained on the basis of 'back-bonding'.

DIAMAGNETIC studies have been proved helpful in the interpretation of structural chemistry of silicon¹. The values of χ_{Si} and χ_{CH_2} calculated for a series of silicon compounds containing Si-O bonds have thrown light on the nature of Si-O bonding. However, very little attention was paid to the compounds containing Si-N bond². Very recently diamagnetic studies of trialkylsilylamidoximes³ and dialkylsilyl derivatives of amidoximes⁴ have been reported. In this note experimental and the calculated values of diamagnetic susceptibility of cyclic dialkylsilylamidoximes (containing both Si-O and Si-N bonds) and the values of χ_{Si} and χ_{CH_2} for these series are being reported and discussed.

Precautions were taken to exclude moisture throughout the experimental manipulations. Freshly prepared and purified samples of dialkylsilylamidoximes⁵ (I) were used for the diamagnetic susceptibility measurements. Benzene was used as a reference liquid having specific susceptibility -0.702×10^{-6} cgs units and all the measurements were carried out at room temperature (38°) by Gouy method. For the theoretical value of molecular susceptibility, a wave mechanical method using the concept of bond susceptibility has been employed⁶⁻⁸.



The experimentally determined and the theoretical values for diamagnetic susceptibility are summarized in Table 1 and exhibit fairly good agreement.

The χ_M values for the compounds Ia and Ib ($n = 1, 2, 3$) reported in Table 1 have been treated graphically by plotting molar susceptibility against

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TABLE 1 — DIAMAGNETIC SUSCEPTIBILITY DATA FOR DIALKYL-SILYLAMIDOXIMES (Ia and b)

R	R'	χ_M^* (obs.)	Diff. (%) between obs. and calc.
COMPOUNDS OF THE TYPE Ia			
Me	Me	81.8	-5.2
Et	Me	93.0	-4.8
Pr	Me	105.0	-4.0
Ph	Me	125.4	-1.6
COMPOUNDS OF THE TYPE Ib			
Me	Et	105.0	-4.0
Et	Et	116.0	-3.6
Pr	Et	127.5	-3.2
Ph	Et	148.2	-1.3

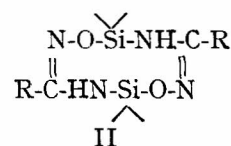
*Numerical values are -10^{-6} cgs units.

TABLE 2 — DIAMAGNETIC SUSCEPTIBILITY OF THE METHYLENE GROUPS AND THE CENTRAL METAL ATOM IN Ia AND Ib

Gradient of plot of χ_M vs n	χ_{CH_2}	Axial intercept	χ_{Si}
COMPOUNDS OF THE TYPE Ia			
11.22	11.22	70.47	17.77
COMPOUNDS OF THE TYPE Ib			
11.26	11.26	93.22	17.80

the length of the alkyl chains in the homologous compounds. Both the plots were linear and the axial intercepts of both give the values of molar susceptibility for the compounds Ia and Ib when $n = 0$. χ_{Si} and χ_{CH_2} (Table 2) have been obtained with the help of these plots using the standard values^{6,9,10}.

The lower values of χ_{Si} (17.77 and 17.80) in comparison to χ_{Si} for Si-C system (reported to be 21.00 for tetra-compounds) is explainable by 'back-bonding' to the silicon atom from oxygen and nitrogen lone-pairs forming ($p \rightarrow d$) π -bonding. These results are consistent with earlier findings for dialkylsilyl derivatives of amidoximes⁴ (systems containing two Si-O bonds). The relatively lower values can be attributed to the lower electronegativity of nitrogen (in comparison to oxygen) permitting relatively stronger π -bonding. Further, these χ_{Si} values are consistent with that for monomeric dialkylsilyl derivatives of amidoximes; supports proposed symmetrical structure (II) for dimeric dialkylsilylamidoximes⁵.



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Ni(II), Ru(III) & Os(VIII) Complexes with Pyrimidines

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Ni(II) and Ru(III) react with 4-amino-6-hydroxy-5-nitroso-2-methylpyrimidine and Ru(III) and Os(VIII) with 2,4,5,6-tetrahydropyrimidine forming coloured complexes suitable for spectrophotometric determination of the metals. Ni(II) and Ru(II) form 1:2 complexes (metal:ligand) while Os(VIII) forms 1:4 complex (metal:ligand). For Ru(III) determination, both the compounds are comparable in sensitivity and selectivity. Formation of Os(VIII) complex with tetraaminopyrimidine (λ_{\max} 490-500 nm; ϵ_{\max} 20000) in the pH range 1.0-5.0 provides a method for its determination which is comparable to well-known methods.

In our investigations to explore the analytical potentialities of pyrimidines¹⁻⁷, we found that pyrimidines are generally useful for the determination of iron and platinum group metals. In the present note, the complexes of Ni(II) and Ru(III) with 4-amino-6-hydroxy-2-methyl-5-nitroso-pyrimidine (λ_{\max} 300, 345 nm; ϵ , 4790, 6420) and Ru(III) and Os(VIII) with 2,4,5,6-tetraaminopyrimidine sulphate (λ_{\max} , 280, 370 nm; ϵ , 10200, 200), are described. These ligands have also been used for the spectro-

photometric determination of Ni(II), Ru(III) and Os(VIII).

Standard solutions of the ligands (Aldrich Chemical Co., USA) were prepared in hot water. Metal solutions were prepared by dissolving NiSO₄·(NH₄)₂SO₄·6H₂O in water, RuCl₃·3H₂O (Koch Light, UK) in 1.0N HCl and OsO₄ (Johnson Matthey, UK) in 0.5N NaOH. The solutions were standardized by recommended procedure. Ru(III) solution was preserved in nitrogen atmosphere to prevent oxidation.

When aqueous solutions of the metal and the ligand were mixed, complex formation took place. The characteristics of the complexes obtained are summarized in Table 1.

TABLE 2 — TOLERANCE LIMITS (ppm) OF DIVERSE IONS IN DETERMINATION OF METALS USING PYRIMIDINOL AND TETRAAMINOPYRIMIDINE

Diverse ion	Pyrimidinol		Tetraaminopyrimidine	
	Ni(II)	Ru(III)	Ru(III)	Os(VIII)
Fluoride	40	500	100	100
Chloride	1000	1000	1000	1000
Bromide	200	1000	1000	1000
Iodide	400	500	1000	1000
Nitrite	80	*	*	*
Nitrate	400	500	500	1000
Perchlorate	800	1000	1000	1000
Thiocyanate	80	500	1000	1000
Acetate	200	1000	1000	1000
Thiosulphate	400	500	500	1000
Oxalate	200	100	100	500
Tartrate	200	500	100	200
EDTA	1	100	15	50
Thiourea	160	50	100	*
Borate	800	500	500	500
Phosphate	200	1000	500	1000
Citrate	200	100	100	1000
Ca(II) or Sr(II)	50	200	150	100
Ba(II)	50	200	150	500
Zn(II)	100	200	150	200
Cd(II)	100	60†	400	250
Hg(II)	*	10‡	100	100
Tl(I)	50	100	200	100
Sn(IV)	*	*	50	50
V(IV)	*	60	20	10
Mn(II)	200	60	100	100
Co(II)	3	60¶	60	150
Ni(II)	—	200	100	100
Pd(II)	5	10	10	10

*Interferes. †Masked with EDTA, ‡Masked with iodide. ¶Masked with thiocyanate.

The presence of Cu(II), Fe(II), Fe(III), Ru(III) or Os(VIII) causes interference.

TABLE 1 — CHARACTERISTICS OF THE METAL COMPLEXES WITH PYRIMIDINES

Characteristic	Pyrimidinol complex with		Aminopyrimidine complex with	
	Ni(II)	Ru(III)	Ru(III)	Os(VIII)
Colour	Yellow	Red	Green	Red
λ_{\max} (nm)	380-390	540	590	490-500
σ_{\max} (litre mole ⁻¹ cm ⁻¹)	6666	13515	15300	20000
Reagent needed for full colour development	15 times	25 times	32 times	10 times
pH range for maximum absorbance	6.5-7.5	4.2-6.8	4.5-6.5	1.0-5.0
Beer's law range ($\mu\text{g/ml}$)	Up to 3.5	Up to 5.5	Up to 6.9	Up to 9.8
Accurate range of determination (ppm)	0.66-2.69	0.79-4.89	0.6-5.9	1.3-9.5
Sandell's sensitivity	0.0058	0.0073	0.0060	0.0090
Composition (metal-ligand)	1:2	1:2	1:2	1:4
Behaviour in organic solvents	Not extractable		Not extractable	
Std devn from 8 samples (metal conc. in ppm; mean absorbance)	0.0015 (2.3; 0.40)	0.0010 (3.95; 0.53)	0.0010 (3.90; 0.60)	0.0020 (4.7; 0.50)