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Studies on Mixed Chelates. VII. Mixed Nickel(II) Chelates Containing *N,N'*- or *N,N*-Dialkylethylenediamines and Acetylacetone

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Twelve mixed nickel(II) chelates with *N,N'*- or *N,N*-dimethyl (or diethyl)ethylenediamines and acetylacetonate ion (acac) were prepared, and their properties were compared with those of the similar chelates with *N,N,N',N'*-tetramethyl(or tetraethyl)ethylenediamine. With the decrease of the number and bulkiness of the *N*-alkyl groups in the diamine, the tendency of forming 6-coordinated mixed chelates remarkably increases. The chelates of the type [Ni(diamine)(acac)]X, formed when X is $B(Ph)_4$, which are essentially similar to the corresponding chelates with *N,N,N',N'*-tetraalkylethylenediamines, but more apt to combine with solvent molecules and to go over into 6-coordinated structures than the latter.

In the previous papers,[1,2] the authors reported that *N,N,N',N'*-tetramethylethylenediamine (tmen) and various β-diketonate ions form two kinds of nickel(II) chelates, *i.e.*, the blue, 6-coordinate, high-spin $[Ni(tmen)(\beta\text{-dik})(OH_2)_2]ClO_4$, $[Ni(tmen)((\beta\text{-dik})NO_3]$ and $[Ni(tmen)(\beta\text{-dik})_2]$ and red, planar 4-coordinate, low-spin $[Ni(tmen)(\beta\text{-dik})]ClO_4$ and $[Ni(tmen)(\beta\text{-dik})]B(Ph)_4$, and an equilibrium is established in organic solutions of the latter chelates:

$$\underset{\text{Red}}{[Ni(tmen)(\beta\text{-dik})]^+} + 2\text{Solv.} \rightleftharpoons \underset{\text{Blue}}{[Ni(tmen)(\beta\text{-dik})(\text{Solv.})_2]^+}$$

(Solv.=solvent molecule). They also studied the chelates containing *N,N,N',N'*-tetraethylethylenediamine (teen) instead of tmen and found generally similar results, but here the planar chelates are more reluctant to go over into 6-coordinate structures, owing to the increased steric hindrance of the larger N-alkyl groups.

In this paper the authors will report on the preparation and properties of similar mixed chelates containing *N,N'*-dimethyl, *N,N*-dimethyl, *N,N'*-diethyl, and *N,N*-diethylethylenediamines (abbreviated as sym-dmen, unsym-dmen, sym-deen and unsym-deen,[3] respectively) and acetylacetonate ion (acac).

Experimental

Preparation of the Chelates. *Chelates of the Type [Ni(diamine)(acac)$_2$](No. I—No. IV in Table 1)*: To an aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mmol), acetylacetone (20 mmol) and an aqueous solution of Na_2CO_3 (5 mmol) are added with stirring. The precipitate formed is dissolved in methanol, and dmen or deen (10 mmol) is added. A blue solution is obtained, from which blue crystals separate out upon concentration and standing. They are recrystallized from 1,2-dichloroethane.

The sym-dmen and sym-deen chelates prepared in this way contain one molecule of crystal water, but the unsym-dmen and unsym-deen chelates are anhydrous.

Chelates of the Type [Ni(diamine)$_2$(acac)]ClO$_4$ (No. V—No. VIII): To a methanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mmol), acetylacetone (10 mmol), Na_2CO_3 (5 mmol), and dmen or deen (10 mmol) are added in succession. The blue solution is filtered, concentrated and let stand, until crystals separate out, which are recrystallized from 1,2-dichloroethane.

Chelates of the Type [Ni(diamine)(acac)]B(Ph)$_4$(No. IX—No. XII): To a methanolic solution of $Ni(NO_3)_2 \cdot 6H_2O$ (10 mmol), acetylacetone (10 mmol), Na_2CO_3 (5 mmol) and sym- or unsym-dmen (10 mmol) are added with stirring in succession. The blue solution is evaporated to driness, and the residue is dissolved in 1,2-dichloroethane and filtered. To this solution, which is expected to contain $[Ni(dmen)(acac)NO_3]$ (*cf.* the preparations of $[Ni\ (tmen)(acac)NO_3]$ and $[Ni\ (teen)(acac)NO_3]$ reported before[1,2]), $NaB(Ph)_4$(14 mmol) is added. A red solution is obtained, which is filtered, concentrated and let stand, until red crystals separate out, which are recrystallized from 1,2-dichloroethane.

The chelates with sym- and unsym-deen are more difficult to prepare. Their 1,2-dichloroethane solutions can be obtained in the same way, but they become syrupy upon concentration. Precipitating with diethyl ether, powder-like mixed chelates can be obtained from them.

Physical Measurements. The methods and instruments used in this study were the same as those in the previous studies of this series.[1,2]

Results and Discussion

The formulas, colors, compositions, and effective magnetic moments of the obtained chelates are shown in Table 1. It is clear that the blue chelates, No. I—No. VIII, are all high-spin, and the red ones, No. IX—No. XII, are all low-spin, and each of them should be formulated as shown. The small magnetic moments of the red chelates are probably due to impurities, since all of them were rather difficult to prepare and purify, and may contain small amounts of high spin chelates.

Formation and Preparation of the Chelates. Although it was tried to get all kinds of mixed chelates corresponding to those obtained before,[1,2] it was found that, with the four dialkyl diamines used in this study, the formation of the chelate species $[Ni(diamine)(acac)_2]$ and $[Ni(diamine)_2(acac)]^+$, *i.e.*, blue, 6-coordinate, high-spin chelates containing three typical chelating ligands, seems to be strongly favored in the reaction mixtures, even when their compositions differ considerably from those of such chelates (*cf.* Experimental), so that only these chelates (the latter in the form of the perchlorates) could be obtained readily in crystalline state. Only in the case where the counter anion is tetraphenylborate, red, planar 4-coordinate and low-spin chelates $[Ni(diamine)(acac)]B(Ph)_4$ were obtained with some

TABLE 1. COLORS, COMPOSITIONS[a], AND MAGNETIC MOMENTS OF THE CHELATES OBTAINED

No.	Chelate	Color	C%	H%	N%	μ_{eff}(B.M.)
I	[Ni(sym-dmen)(acac)$_2$]·H$_2$O	Blue	46.11(46.30)	8.10(7.79)	7.64(7.72)	3.09
II	[Ni(unsym-dmen)(acac)$_2$]	Blue	48.48(48.73)	7.78(7.59)	8.08(8.12)	3.37
III	[Ni(sym-deen)(acac)$_2$]·H$_2$O	Blue	49.51(49.12)	8.31(8.26)	7.36(7.16)	3.13
IV	[Ni(unsym-deen)(acac)$_2$]	Blue	51.87(51.50)	8.03(8.10)	7.59(7.51)	3.13
V	[Ni(sym-dmen)$_2$(acac)]ClO$_4$	Bluish Violet	36.07(36.01)	7.40(7.22)	12.93(12.92)	3.05
VI	[Ni(unsym-dmen)$_2$(acac)]ClO$_4$	Blue	35.68(36.01)	7.44(7.22)	12.32(12.92)	3.10
VII	[Ni(sym-deen)$_2$(acac)]ClO$_4$	Blue	41.86(41.70)	8.45(8.03)	11.35(11.44)	3.12
VIII	[Ni(unsym-deen)$_2$(acac)]ClO$_4$	Blue	41.28(41.70)	8.28(8.03)	11.11(11.44)	3.12
IX	[Ni(sym-dmen)(acac)]B(Ph)$_4$	Red	69.41(70.13)	6.80(6.96)	4.96(4.95)	0.34
X	[Ni(unsym-dmen)(acac)]B(Ph)$_4$	Red	69.14(70.13)	6.87(6.96)	4.69(4.72)	0.52
XI	[Ni(sym-deen)(acac)]B(Ph)$_4$	Red	70.02(70.86)	7.46(7.31)	4.60(4.72)	0.75
XII	[Ni(unsym-deen)(acac)]B(Ph)$_4$	Red	68.14(70.86)	7.25(7.31)	4.53(4.72)	0.32

a) Calculated values in parentheses.

difficulty.*

It may be noted that the chelates of the type [Ni(diamine)$_2$(acac)]X can be prepared with dmen's and deen's but not with tmen and teen, while those of the type [Ni(diamine)(acac)$_2$] can be prepared with any of these diamines. This is undoubtedly due to the fact that the stability of a former type chelate depends critically on the magnitude of the large steric repulsion between two bulky diamines in it, while that of a latter type chelate does not depend so strongly on the bulkiness of the diamine since acac is a ligand of much smaller steric requirement.

Electronic Spectra. As in the case of the tmen and teen chelates, all these chelates are soluble in most organic solvents. The ν_{max} and ε_{max} values in the electronic spectra of such solutions, and the ν_{max} values in the reflection spectra of the solid chelates, are summarized in Tables 2 and 3.

The features of these spectra are in general very similar to those of the tmen- and teen-containing chelates.[1,2] All the high-spin chelates show two weak bands in the visible and near infrared regions, which move only little in going from the solid to the solutions

TABLE 2. $\nu_{max}/(10^3\text{cm}^{-1})$ AND ε_{max}[a] OF THE HIGH-SPIN CHELATES OBTAINED

No.	Solid	ClCH$_2$CH$_2$Cl	Ethanol	DMF
I		10.00(12.8)	10.13(10.8)	10.05(11.8)
	16.81	16.53(7.8)	16.84(7.4)	16.75(7.7)
II		9.80(14.8)	9.83(10.8)	9.80(12.3)
	16.56	16.47(11.1)	16.50(7.4)	16.42(8.5)
III		9.85(12.4)	9.97(10.7)	9.90(11.8)
	16.56	16.53(7.8)	16.64(7.4)	16.56(7.7)
IV		9.62(11.1)	9.57(9.7)	9.62(10.1)
	16.61	16.31(7.1)	16.26(6.9)	16.29(7.0)
V		10.59(10.6)	10.49	10.58(11.2)
	17.24	17.35(8.4)	17.21	17.30(8.7)
VI		9.70(11.5)	9.76(11.2)	9.80(11.7)
	17.01	17.18(7.6)	16.84(7.2)	16.81(7.6)
		20.49(7.9)		
VII		10.34(10.9)	10.26	10.21(11.8)
		17.09(9.2)	16.92	16.95(8.5)
VIII		8.42(13.1)	8.46	8.66(9.8)
	16.92	16.95(5.7)	16.72	16.61(6.2)
		20.53(3.5)	20.92 vw	

a) In parentheses.

TABLE 3. $\nu_{max}/(10^3\text{cm}^{-1})$ AND ε_{max}[a] OF THE LOW-SPIN CHELATES OBTAINED

No.	Solid	ClCH$_2$CH$_2$Cl	Acetone	Ethanol	DMF
IX			10.00 (9.6)	10.12(8.5)	10.18(9.4)
			16.61 (9.0)	16.47(6.5)	16.64(7.6)
	20.58	20.88(113)	20.70 (8.4)		
X			9.39 (8.0)	9.80(11.5)	9.83(9.9)
			16.08 (10.5)	16.39(9.2)	16.34(7.7)
	20.36	20.75(120)	21.37 (13.4)		
XI			9.90 (8.1)	9.90(8.7)	9.98(8.8)
			16.56 (9.6)	16.13(9.5)	16.64(8.7)
	20.66	20.79(110)	20.62 (19.6)	20.58 sh	20.49 vw
XII			7.38[b](10.0)	9.40(7.0)	9.62(8.1)
			15.72[b](16.1)	16.23(7.1)	16.29(7.6)
	20.70	20.62(122)	20.92 (36.0)	20.88 sh	

a) In parentheses. b) These very low values may be taken as an indication for the large interligand repulsion in the chelate [Ni(unsym-deen)(acac)(acetone)$_2$] which weakens the Ni-acetone bonds so much.

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* The possibility that the chelates X and XII with unsym-diamines are, in fact, Schiff base chelates, *e.g.*, [Ni{NR$_2$-(CH$_2$)$_2$N=C(CH$_3$)CHCOCH$_3$} (OH$_2$)]B(Ph)$_4$ with the same compositions as the mixed chelates, can be ruled out, because the NMR spectra of these chelates are clearly in support of the mixed chelate formulation.[4]

in various solvents.** This fact shows that the structures of these 6-coordinate chelates are stable enough in solution and not influenced sensitively by the solvents used.

Comparison of the spectra in 1,2-dichloroethane, in which the interaction with the solutes will be the least, shows that, in each of the two series of the 6-coordinate chelates, the ν_{max} of the two bands decrease in the order (1) of the diamines:

$$\text{sym-dmen} > \text{sym-deen} \gtrsim \text{unsym-dmen} > \text{unsym-deen} \qquad (1)$$

indicating that the ligand field strength (l.f.s.) in these chelates also decreases in this order. It may also be noted that, among the chelates of the type $[\text{Ni(diamine)}_2\text{(acac)}]\text{X}$, the decrease in ν_{max} is quite large (10590 cm^{-1} to 8420 cm^{-1} in ν_1, which is a direct measure of 10Dq), while among those of the type $[\text{Ni(diamine)(acac)}_2]$ it is much smaller (10000 to 9620 in ν_1), showing that the l.f.s in a former type chelate is much more sensitive to the steric change of its diamine than that in a latter type one, in comformity with the view on their ease of formation mentioned above.

On the other hand, the spectra of the red, 4-coordinate and low-spin chelates are influenced strongly by the solvent, but the mode of the spectral change observed is essentially the same as that observed among the corresponding chelates of tmen or teen, indicating that here again the equilibrium

$$\underset{\text{I}}{[\text{Ni(diamine)(acac)}]^+} + 2\text{Solv.} \rightleftharpoons \underset{\text{II}}{[\text{Ni(diamine)(acac)(Solv.)}_2]^+}$$

is established in solution, which is shifted from the left hand side to the right as follows (Figs. 1 and 2):

$$\underset{\approx 100\%\ \text{I}}{\text{1,2-dichloroethane}} \longrightarrow \underbrace{\text{Acetone} \longrightarrow \text{Ethanol}}_{\text{I+II}} \longrightarrow \underset{\approx 100\%\ \text{II}}{\text{DMF}}$$

Increase in II (dearease in I) ⟶

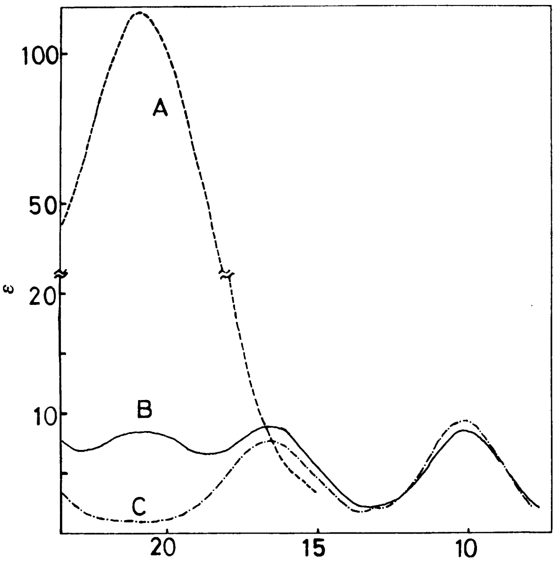

Fig. 1. Electronic spectra of the chelate IX in three solvents.
A: 1,2-Dichloroethane; B: acetone; C: DMF.

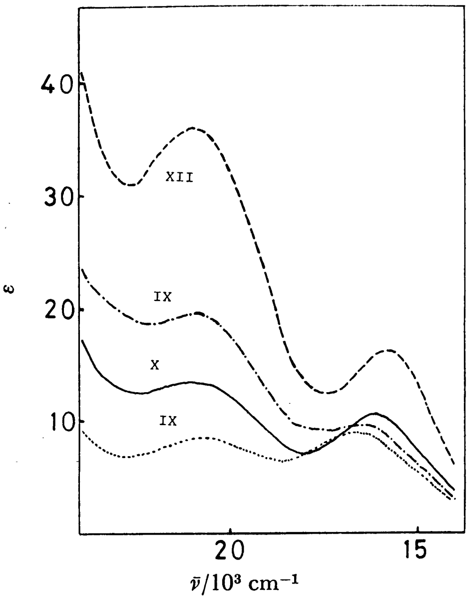

Fig. 2. Comparison of the electronic spectra of the chelates IX—XII in acetone.

TABLE 4. PERCENTAGES OF $[\text{Ni(diamine)(acac)}]^+$, REMAINING UNSOLVATED IN THE EQUILIBRIUM MIXTURES PRODUCED BY DISSOLVING THE CHELATES IX—XII AND THEIR tmen- AND teen- CONTAINING ANALOGUES IN ACETONE

IX	7.5%	$[\text{Ni(tmen)(acac)}]\text{B(Ph)}_4$ [a]	21%
X	11.0	$[\text{Ni(teen)(acac)}]\text{B(Ph)}_4$ [a]	82
XI	18.0		
XII	30.4		

a) *Cf.* Ref. 2.

As in the case of the teen chelates,[2] it is possible to calculate the percentages of I in the equilibrium mixtures. From the data in Fig. 1, the values in Table 4 are obtained. The values for the corresponding tmen and teen chelates are also shown. It can be seen that the tendencies of these chelates to combine with solvent molecules and to go over into 6-coordinate structures decrease in the order:

$$\text{sym-dmen} > \text{unsym-dmen} > \text{sym-deen} \approx \text{tmen} > \text{unsym-deen} \gg \text{teen} \qquad (2)$$

It is interesting to note that this order (2) is nearly the same as the order (1) of the decreasing l.f.s. in octahedral chelates.*** The relative positions of tmen and teen in the order (1), which can be found by comparing the data of the chelates of the type $[\text{Ni(diamine)(acac)}_2]$ with those of $[\text{Ni(tmen)(acac)}_2]$ and $[\text{Ni(teen)(acac)}_2]$,[1,2] are also nearly the same as their positions in the order (2), except that tmen lies between teen and unsym-deen.

** The solid reflection spectra could be measured only up to 700 nm so that the first band is lacking in them.

*** In fact, there is also a slight shift of ν_{max} values of the planar $[\text{Ni(diamine)(acac)}]\text{B(Ph)}_4$ chelates in 1,2-dichloroethane in the order (1), showing that here too the l.f.s. decreases in this order.

These facts can be understood as follows: the total volume of the *N*-alkyl groups in a diamine increase naturally in the order:

teen > unsym-deen, sym-deen > unsym-dmen, sym-dmen

The position of tmen in this series will be somewhere near the deen's. Now if it is assumed that the amount of steric hindrance, which a neighboring ligand suffers from such groups in an unsym-diamine chelate, is somewhat larger than that in its sym-diamine analogue, the order (1) or (2) can be taken as the inverse order of such steric hindrance in each case. Thus the order (1) indicates that the l.f.s. in an octahedral chelate is weakened owing to the increasing interligand repulsion, and the order (2) that the coordination of solvent molecules above and below a planar chelate is hindered more and more owing to the increasing ligand-solvent repulsion.

It is also of interest to note that a weak band at 20000 to 21000 cm^{-1} is observed in some spectra of the chelates VI and VIII, indicating the formation of the species [Ni(diamine)(acac)]$^{+}$, or, in other words, the dissociation of a diamine molecule from the chelate cation, in solvents of lower coordination ability. Only the chelates of the type [Ni(diamine)$_2$(acac)]X (and not those of the type [Ni(diamine)(acac)$_2$]) show such a band, and only the unsym-diamine chelates do so, suggesting that here also interligand repulsion is playing a role.

Table 5. Examples of ν_{CO}, $\nu_{C=C}$, and $\Delta\nu$ in the two types of chelates (cm^{-1})

Chelate	ν_{CO}	$\nu_{C=C}$	$\Delta\nu$	Spin type
II	1604	1514	90	High Spin
IV	1596	1516	80	
V	1597	1525	72	
VI	1586	1507	79	
XI	1578	1528	50	Low Spin
XII	1570	1525	45	

Infrared Spectra. As in the case of the tmen and teen chelates, there are two strong bands at 1500—1600 cm^{-1}, which are ascribed to the C=C and C=O vibrations of acac, and their separations ($\Delta\nu$) are much larger in the 6-coordinate chelates than in 4-coordinate ones (Table 5). It was also found that ClO_4^- ions are not coordinated. In addition, there is N–H stretching absorption at *ca.* 3200 cm^{-1}, which is a single peak in the sym-, but split into two or three peaks in unsym-diamine chelates. The hydrated chelates show also O–H stretching absorption superposed on it, broadening the peak considerably.

In conclusion it can be said that, in going from tmen and teen to the dmen's and deen's, both the l.f.s. in octahedral chelates and their ease of formation (either from component ligands, or from a planar chelate and solvent molecules) remarkably increase, owing to the decrease in steric hindrance caused by the *N*-alkyl groups.

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3) Recently, Fabbrizzi *et al.* (L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, **13**, 3019 (1974)) reported some interesting observations on the thermochromic Cu(II) and Ni(II) chelates of this ligand.

4) Y. Fukuda, unpublished work.