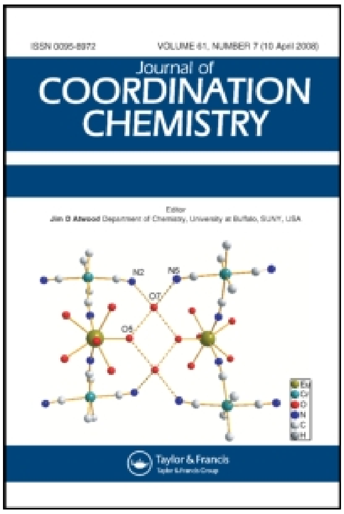

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Linert, W. , Jedlicka, R. , Jameson, R. F. and Gutmann, V.(1988) 'ENTHALPIC AND ENTROPIC CONTRIBUTIONS TO SOLVATOCHROMISM OF NICKEL(II) COMPLEXES', Journal of Coordination Chemistry, 17: 4, 347 — 354

To link to this Article: DOI: 10.1080/00958978808073927

URL: http://dx.doi.org/10.1080/00958978808073927

J. Coord. Chem. 1988, Vol. 17. pp. 347–354
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ENTHALPIC AND ENTROPIC CONTRIBUTIONS TO SOLVATOCHROMISM OF NICKEL(II) COMPLEXES

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(Received November 17, 1987)

Equilibrium constants for the formation of octahedral complexes from square planar nickel(II) complexes with tetramethylenediamine (tmen) and β-diketones have been measured in dichlorethane at different temperatures. The several octahedral complexes are formed by the addition of two molecules of acetone, methanol, ethanol, *n*-propanol and *n*-butanol, respectively. All these donor solvents give rise to isoequilibrium (isokinetic) behaviour, but fall into two distinct groups, namely (*i*) true isokinetic behaviour for ethanol, *n*-propanol and *n*-butanol and (*ii*) isoentropic behaviour for acetone and methanol.

Keywords: Nickel(II), complexes, solvatochromism, tetramethylendiamine, β-diketones

INTRODUCTION

Mixed Ni(II)-complexes with tetramethylenediamine (tmen) and β-diketones (β-dik) such as acetylacetonate (acac), benzoylacetonate (bzac) and dibenzoylacetonate (dbac) are known to show solvatochromism in different solvents (L).[1-7] Spectral analysis has shown[1] that the observed colour change is due to the equilibrium reaction (*1*).

$$\underset{\text{red, square planar}}{[\mathrm{Ni(tmen)(\beta\text{-}dik)}]^+} + 2\mathrm{L} \rightleftharpoons \underset{\text{blue, octahedral}}{[\mathrm{Ni(tmen)\beta\text{-}dik)L_2}]^+} \qquad (1)$$

In weak donor solvents such as 1,2-dichlorethane (DCE) or nitroethane (NE) the square planar form is present, whereas in strong donors, for example in ketones and aliphatic alcohols, the octahedral form predominates. The equilibrium constants for different β-diketones are strongly solvent- and temperature-dependent. It is known that linear relationships exist between the equilibrium constants and donor numbers for the nickel(II) complexes as well as for the analogous copper(II) complexes.

EXPERIMENTAL

$[\mathrm{Ni(tmen)(\beta\text{-}dik)]ClO_4}$ complexes were prepared according to the method of Fukuda.[1] For $[\mathrm{Ni(tmen)(\beta\text{-}dik)]Ph_4B}$ a slightly modified procedure was chosen.[1,7] The elemental analyses of the products are given in Table I. The solvents and ligands were purified using standard procedures.[8-10] The water content in the solvents was measured by Karl-Fischer titration and usually found to be below 30 mg dm^{-3}.

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TABLE I

Melting points, molecular weights and analyses of mixed Ni(II)-complexes (Ni(tmen)(β-dik)BPh_4 with tetramethylethylenediamine (tmen), acetylacetone (acac), benzoylacetone (bzac) and dibenzoylmethanat (dbm).

β-dik	°C	Molecular-weight		%C	%H	%N
acac	176–180	594.28	calc.	70.86	7.31	4.72
			found.	70.91	7.33	4.81
bzac	218[a]	655.33	calc.	73.33	7.01	4.31
			found.	73.31	6.93	4.27
dbm	207[a]	717.40	calc.	75.34	6.60	3.90
			found.	74.99	6.67	3.95

[a] with decomposition.

RESULTS AND DISCUSSION

The spectra of the square planar form (in DCE) and the octahedral form (in MeOH) of the investigated complexes are given in Figs. 1 and 2 and the existence of an isosbestic point in Fig. 1 strongly suggests the presence of only two absorbing species. No significant shifts of the maxima were found for different β-diketones but the extinction coefficients increased with increasing size of these ligands (Table II).

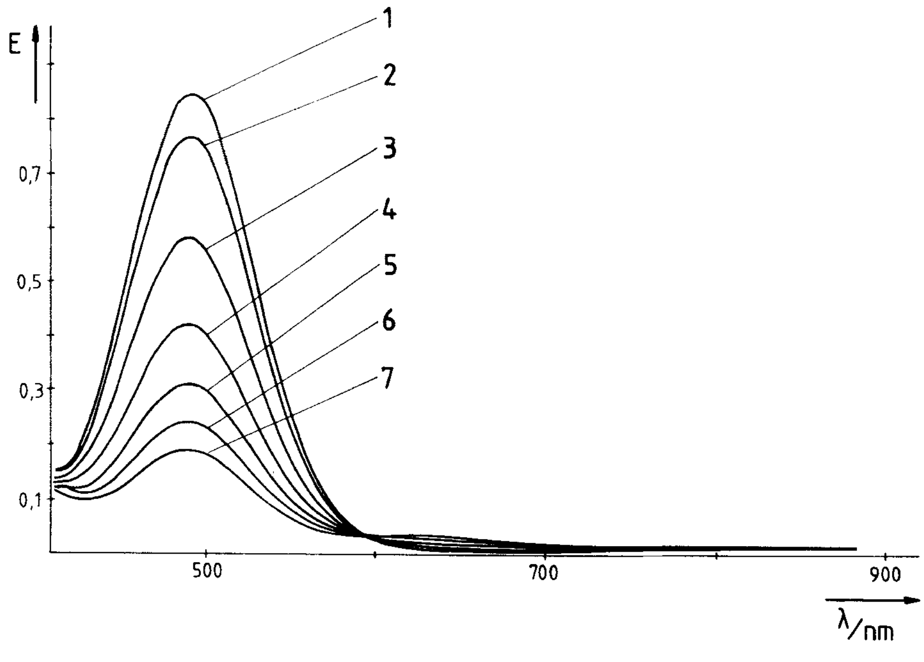

FIGURE 1 Visible region spectra of a 10^{-3} molar solution of Ni(tmen)(acac)BPh_4 in DCE using different MeOH concentrations (1 to 7 refer to 0; 0.45; 0.86; 1.25; 1.6; 1.93; 2.24 molar MeOH in DCE respectively).

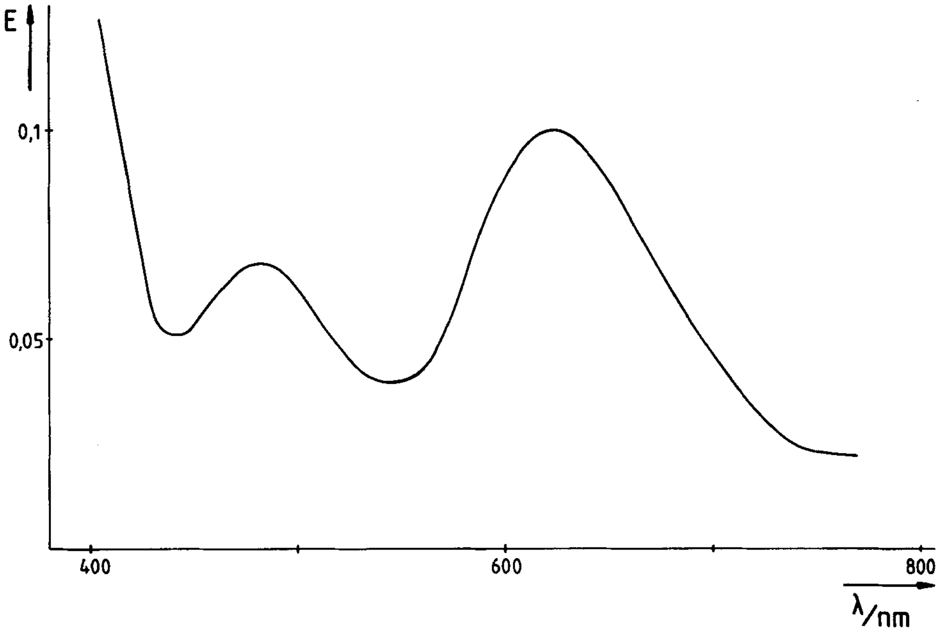

FIGURE 2 Visible region spectrum of a 10^{-2} molar solution of Ni(tmen)(acac)BPh_4 in a 10 molar solution of MeOH in DCE.

The red square planar complex shows only one absorption band in the investigated region positioned at 484 nm. This transition can be assigned[11] either to an $^1A_{1g} \leftarrow {}^1A_{2g}$ ($d_{x^2-y^2}$ to d_{xy}) or to an $^1A_{1g} \leftarrow {}^1B_{2g}$ (d_{z^2} to $d_{x^2-y^2}$) transition. The latter can be excluded by the observation that the band is not shifted when the solvent is changed (Figure 1) which would strongly influence the d_z2-energy level. For the octahedral complex, two of the expected three bands are found in MeOH solution (Figure 2) which can be assigned to a $^3A_{2g} - {}^3T_{1g}(F)$ transition at 620 nm and a $^3A_{2g} - {}^3T_{1g}(P)$ transition at 485 nm (one would expect the third band to be at about 1000 nm, outside the range of these measurements). The central band, at 620 nm, is the one band common to all observed spectra and is therefore the only absorbtion band quoted in Table II.

All these transitions are formally forbidden, their intensity depending on the degree of vibronic interaction. This is in agreement with the observed increase of the extinction coefficients with increasing bulk of the ligands (which in turn leads to an increase in vibrational degrees of freedom).

TABLE II
Absorption maxima (λ_{max}) and extinction coefficients (ε) of the square planar Ni-complexes (in DCE) and the octahedral nickel(II) complexes (in MeOH).

	square planar		octahedral	
β-dik	λ_{max}/nm	ε/dm^2mol^{-1}	λ_{max}/nm	ε/dm^2mol^{-1}
acac	484	1350	620	66
bzac	484	1700	620	70
dbm	484	2400	620	77

The spectral properties of both species do not change significantly with the solvent. This is the crucial difference between the solvato- and thermochromism of these Ni(II)-complexes and those of the analogous Cu(II)-complexes. The copper complexes show a continuous shift of the positions of visible absorption lines with different solvents and with temperature[6] whereas the corresponding nickel complexes show the spectra of two distinct coordination compounds. This difference can be explained by the strong Jahn–Teller effect present in the copper complexes where a tetragonally distorted octahedral configuration is stabilised due to the lifting of the degeneracy of both the e_g and the t_{2g} orbitals. The continuous shift of the absorption lines with changing donor properties of the ligand L is therefore due to a change in the splitting of the d_{xy} and the $d_{x^2-y^2}$ levels. Contrary to this, Ni(II) shows only a second-order Jahn–Teller effect meaning that in general only *either* a square planar *or* an octahedral configuration is stable without the possibility of stable forms between these.

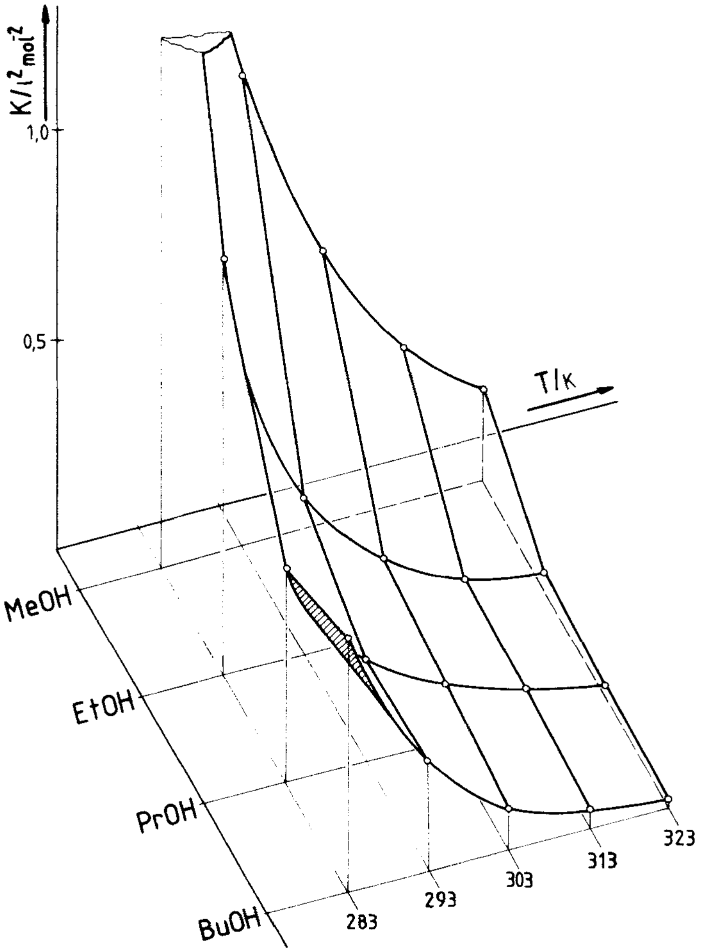

FIGURE 3 Variation of the equilibrium constant with the alcohols and the temperature.

It is obvious, however, that the reaction (*1*) is an approximation of a two-step process. In DCE measurements, the appearence of a single isosbestic point and the independence of calculated equilibrium constants with concentration shows that the concentration of a Ni(tmen)β-dik)L$^+$ species is indeed negligibly small. The equilibrium constants measured in DCE assuming reaction (*1*) are given in Table III. The values increase with increasing molecular weight of the β-dik but decrease with the size of the ligand L when alcohols are compared. In Fig. 3 this is exemplified for Ni(tmen)(acac)BPh$_4$ complexes. In other words, the larger the β-dik and the stronger the electron properties of L the better the octahedral complex is stabilised.

TABLE III
Equilibrium constants for the conversion of the square planar and octahedral configuration of the Ni-complexes with different ligands L at different temperatures in DCE.[a]

β-dik	238 K	293 K	303 K	313 K	323 K
			L = Ac		
acac	0.054	0.031	0.019	0.013	—
bzac	0.170	0.104	0.064	0.038	—
dbm	0.540	0.310	0.177	0.105	0.065
			L = MeOH		
acac		1.15	0.65	0.37	0.22
bzac		2.88	1.66	1.05	—
dbm		6.30	3.55	1.73	1.00
			L = EtOH		
acac		0.376	0.184	0.079	0.045
bzac		0.773	0.383	0.169	0.105
dbm		1.347	0.630	0.217	0.173
			L = PrOH		
acac		0.224	0.133	0.075	0.033
bzac		0.492	0.268	0.150	0.086
dbm		0.880	0.443	0.217	0.122
			L = BuOH		
acac		0.210	0.100	0.050	0.028
bzac		0.650	0.300	0.130	0.070
dbm		0.909	0.478	0.235	0.131

[a] dm^{6}mol^{-2}.

All equilibrium constants measured in DCE decrease with increasing temperature showing the exothermic character of reaction (*1*). Van't Hoff plots (*i.e.*, lnK *versus* 1/T) of the temperature-dependent equilibrium constants exhibit straight lines ($r > 0.99$). The corresponding reaction enthalpies and entropies are collected in Table IV. The van't Hoff lines of reactions measured with Ac and MeOH show isoentropic behaviour, *i.e.*, a common point of intersection at a reciprocal isokinetic temperature near zero (see Fig. 4). (For the statistical analysis showing whether isokinetic behaviour is present or not see ref. 11.) In the case of EtOH, PrOH and BuOH a common point of intersection at an isokinetic temperature (T_{iso}) of 223.7 K is found (see Fig. 5). The observation that these reactions split into two distinct series, one isoentropic containing small sized L, the second one with a real compensation behaviour including L with longer C-chains can be discussed in the following terms. Either the molecular vibrations are almost frozen for (the small) Ac and MeOH in the investigated temperature range, whereas for the larger alcohols additional degrees of vibrational freedom are available, or Ac and MeOH are much less strongly solvated in DCE (*i.e.*, they are much more hydrophilic) than the larger alcohols. Both effects are in fact closely related and both lead one to expect a corresponding change of microscopic degrees of freedom in turn influencing the entropy changes of the reaction in the same way. A relationship between T_{iso} and such degrees of freedom has been proposed,[14,15], which shows, after reinterpreting these results to apply to equilibrium systems, T_{iso} to be proportional to the reciprocal of the change in degrees of freedom between reactants and products. If this change is negligible, as would result from the above assumption, T_{iso} would become very large which is equivalent to isoentropic behaviour. Such an interpretation would also agree with the larger entropy changes found for the series including EtOH, PrOH and BuOH (ΔS between -162 and -206 Jmol^{-1}K^{-1}) compared to the Ac and MeOH series (ΔS about -150 mol^{-1}K^{-1}).

TABLE IV
Reaction enthalpies ΔH^0 [kJmol^{-1}] and reaction entropies ΔS^0 [Jmol^{-1}K^{-1}] for reaction (*1*).

β-dik	Ac		MeOH		EtOH		PrOH		BuOH	
	ΔH^0	ΔS^0	ΔH^0	ΔS^0	ΔH^0	ΔS^0	ΔH^0	ΔS^0	ΔH^0	ΔS^0
acac	−35.6	−150	−43.5	−147	−57.4	−205	−51.2	−184	−59.0	−186
bzac	−36.6	−144	−38.5	−123	−51.2	−177	−45.8	−162	−59.3	−206
dbm	−40.3	−148	−49.2	−152	−53.9	−184	−52.3	−182	−51.3	−176

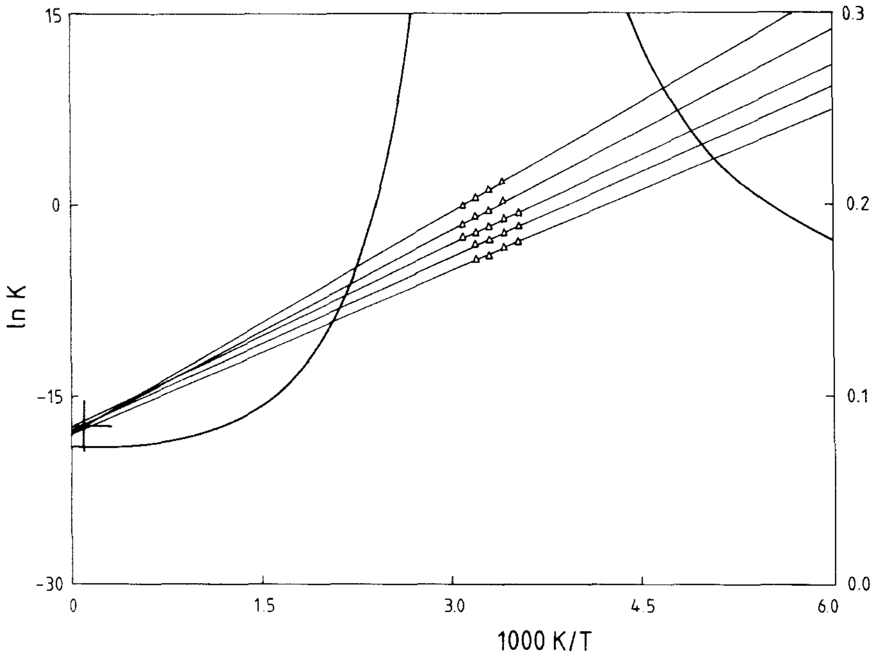

FIGURE 4 Van't Hoff plots for the equilibrium constants for complex formation between different Ni(tmen)(β-dik)$^+$ complexes (with Ac and MeOH).

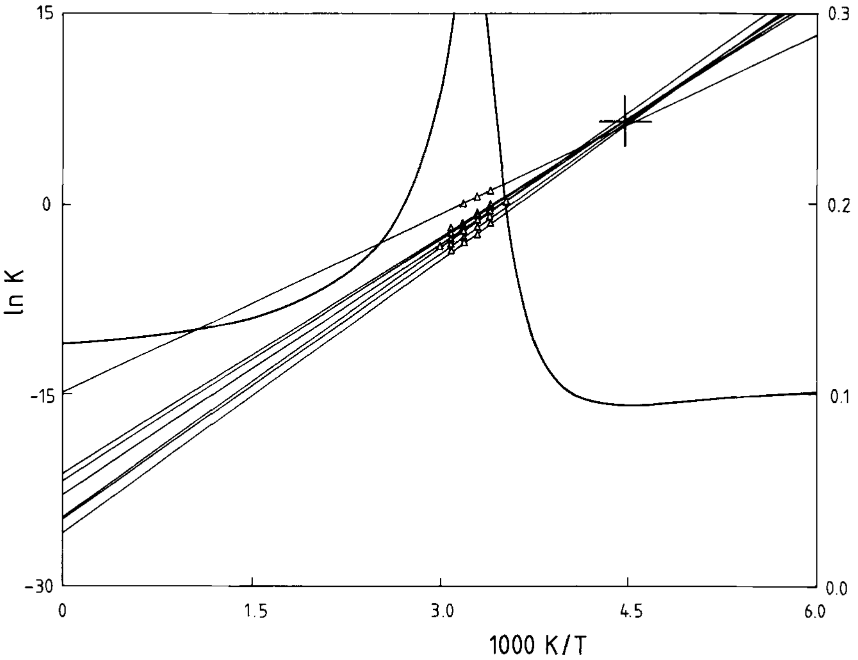

FIGURE 5 Van't Hoff plots for the equilibrium constants for complex formation between different Ni(tmen)(β-dik)$^+$ complexes (with EtOH, PrOH and BuOH).

However, the theoretical description of the IKR as the result of a vibrational interaction between reactants and their molecular surroundings[16] provides a relation between T_{iso} and an active vibrational frequency of the solvent:

$$T_{iso} = h\nu/k_B \qquad (2)$$

For the non-isoentropic reaction series this would give a vibrational frequency of 155 cm^{-1}. The IR-spectrum of DCE shows a strong band at 135 cm^{-1} with a shoulder at 155 cm^{-1} (the same situation is found in the corresponding Raman spectrum). This agreement between required and observed absorbance frequencies is in fact found for some 50 homogeneous[7,16] and heterogeneous[17] reaction series for which Eqn. (*2*) holds.

One final problem concerning the measurements in nitroethane (NE) remains however, and that is that considerable amounts of the five-coordinate Ni(tmen)(β-dik)L$^+$ must be allowed for. The equilibrium constants for the two-step process in this solvent required to fit the data are separable, namely 1.0 M^{-1} and 4.0 M^{-1} for K_1 and K_2, respectively. This difference between DCE and NE may be ascribed to different solvation behaviour of the two solvents; NE, which has obviously stronger coordinating properties than DCE seems to be able to stabilise a species like Ni(tmen)(β-dik)L$^+$ by weak coordination. The influence of the anion on the spectral properties and conductivity measurements[18] suggest a strong ion-pair interaction between Ni(tmen)(β-dik)L$^+$ and the anion. This interaction is of course much weaker than that with the strong donors L. Of course there will always be the question as to the nature of the square planar complex present in weakly coordinating solvents, in other words the extent to which solvent molecules should be considered ligands, albeit very weakly bound.

ACKNOWLEDGEMENTS

Thanks are due to Dr. K. Hassler and Dr. G. Leising (Technical University of Graz, Austria) for measuring Raman and far IR-spectra and to the "Fonds zur Förderung der wissenschaftlichen Forschung" (project 5443) and to the "Hochschuljubiläumsstifung der Stadt Wien" for financial support.

REFERENCES

1. Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem.*, **34**, 2315 (1972).
2. Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem.*, **37**, 455 (1975).
3. N.T. Nga, Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jap.*, **50**, 154 (1977).
4. N. Hoshino, Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jap.*, **54**, 420 (1981).
5. Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jap.*, **43**, 2282 (1970).
6. R.W. Soukup and R. Schmid, *J. Chem. Ed.*, **62**, 459 (1985).
7. W. Linert, B. Pouresmail and V. Gutmann, *J. Coord. Chem.*, in press.
8. M. Bestemer, *Angew. Chem.*, **63**, 118 (1951).
9. "Organikum", 16th Edn., VEB Deutscher Verlag der Wissenschaften, Berlin (1986).
10. G.B. Porter and V. Hanten, *J. Inorg. Chem.*, **18**, 2053 (1979).
11. D.J. MacDonald, *Inorg. Chem.*, **6**, 2269 (1967).
12. F.A. Cotton and G. Wilkinson, "Anorganische Chemie" (Verlag Chemie, Weinheim, 1980).
13. W. Linert, *Inorg. Chim. Acta*, **141**, 233 (1988).
14. W. Linert, A.B. Kurdrjawtsev and R. Schmid, *Aust. J. Chem.*, **36**, 1903 (1983).
15. W. Linert, A.B. Kurdrjawtsev, *Aust. J. Chem.*, **37**, 1139 (1984).
16. W. Linert, *Chem. Phys.*, **114**, 449 (1987); **114**, 457 (1987); **116**, 381 (1987).
17. W.C. Conner and W. Linert, submitted for publication.
18. W. Linert, *Inorg. Chim. Acta*, **132**, 81 (1987).