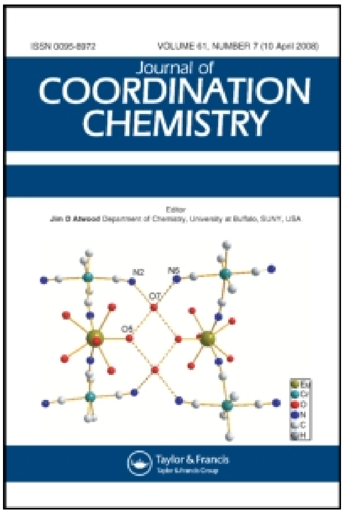

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and dynamic stereochemistry of thermochromic tris(dithiocarbamato)vanadium(III) complexes stereochemistry of thermochromic tris(dithiocarbamato)vanadium(III) complexes

Subrato Bhattacharya[a]; Bikram K. Kanungo[b]; Suban Sahoo[b]
[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 233 001, India [b] Department of Chemistry, S.H.S. Central Institute of Engineering and Technology, Longowal 148 106, India

To cite this Article Bhattacharya, Subrato , Kanungo, Bikram K. and Sahoo, Suban(2006) 'Synthesis, characterization and dynamic stereochemistry of thermochromic tris(dithiocarbamato)vanadium(III) complexes stereochemistry of thermochromic tris(dithiocarbamato)vanadium(III) complexes', Journal of Coordination Chemistry, 59: 4, 371 — 378

To link to this Article: DOI: 10.1080/00958970500240110

URL: http://dx.doi.org/10.1080/00958970500240110

Journal of Coordination Chemistry
Vol. 59, No. 4, March 2006, 371–378

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization and dynamic stereochemistry of thermochromic tris(dithiocarbamato)vanadium(III) complexes

SUBRATO BHATTACHARYA*†, BIKRAM K. KANUNGO‡
and SUBAN SAHOO‡

†Department of Chemistry, Faculty of Science, Banaras Hindu University,
Varanasi 233 001, India
‡Department of Chemistry, S.H.S. Central Institute of Engineering and Technology,
Longowal 148 106, India

(*Received in final form 2 December 2004*)

The vanadium(III) complexes, $V(S_2CNMe_2)_3$ (**1**) and $V(S_2CN^iPr_2)_3$ (**2**) were prepared and characterized by analysis, IR, electronic and ^1H NMR spectra. The complexes show reversible thermochromic behaviour. MM2 calculations were used to simulate the molecular structure of **1**. For **2**, variable temperature ^1H NMR revealed hindered rotation about C–N bonds. The rotational energy barrier ($38\,kJ\,mol^{-1}$) was obtained by molecular mechanics force-field calculations.

Keywords: Dithiocarbamate; Thermochromism; Vanadium(III); Variable temperature spectra; Structure simulation

1. Introduction

Complexes of dithiocarbamates with transition metals have been studied extensively due to the versatility of the ligands [1]. The ligands form highly stable complexes with all types of metal ions irrespective of their hard or soft character. It has been reported earlier that dithiocarbamates can stabilize unusual coordination environments with group 13 metal ions [2]. It has been observed that hydrocarbon frameworks with delocalized π electron density (including benzene) possess intermolecular interactions through π stacking [3]. Sulphur donor atoms and extensive delocalized π density in dithiocarbamato complexes could be a potential source of charge transfer-intermolecular (weak) bonding. Such interactions in other systems are known to lead to interesting properties. For example, several Schiff base ligands with intermolecular π interactions are known to exhibit thermochromic behaviour [4] and disulfide bridged

---

*Corresponding author. Email: s_bhattacharya@sancharnet.in

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500240110

dithiolate complexes of molybdenum show photochromism [5]. Here, the synthesis and characterization of thermochromic vanadium(III) complexes of dialkyldithiocarbamates are reported including variable temperature electronic spectroscopic and NMR studies. Few dithiocarbamate complexes of V(III) and V(IV) have been reported [6–9] and their thermochromic properties have not been studied.

2. Experimental

Solvents were dried and distilled before use. All experimental manipulations were carried out under a dry dinitrogen atmosphere. Vanadium trichloride was obtained from Aldrich and used as such. Sodium salts of dimethyl and diisopropyldithiocarbamate were prepared by previously reported procedures [10, 11]. Vanadium and sulphur were estimated gravimetrically as silver vanadate and barium sulphate, respectively. C, H, N were estimated microanalytically using a Perkin–Elmer 240c analyzer. IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Jasco FX90Q and Perkin–Elmer RX-1000 FT-IR spectrophotometers. Electronic spectra were recorded at various temperatures using an Agilent 8453 diode array spectrophotometer attached to a Julabo FT-901 cooling system. ^{1}H NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as internal reference using a JEOL FX-90Q spectrometer.

2.1. *Preparation of complexes*

A solution of sodium dimethyl- or diisopropyldithiocarbamate in ethanol ($\sim$20 cm^3) was added to a solution of vanadium trichloride in ethanol ($\sim$10 cm^3) in a 1 : 3 mol ratio with stirring at room temperature (27°C). After stirring for $\sim$2 h the precipitate that had formed was filtered off and dried under reduced pressure for 1 h at 30°C and 0.01 mmHg. The product was recrystallized from benzene/*n*-hexane (1 : 1).

3. Results and discussion

3.1. *Syntheses*

Reactions of vanadium(III) chloride with the sodium salt of dimethyl- or diisopropyldithiocarbamate in ethanol yielded the corresponding tris(dithiocarbamato) vanadium(III) complexes, $V(S_2CNMe_2)_3$ (**1**) and $V(S_2CN^iPr_2)_3$ (**2**) in good yields. Satisfactory analyses were obtained for the stoichiometries given. The complexes are yellow-brown solids that are soluble in common organic solvents. Both complexes are thermally stable but on exposure to open atmosphere their colour changes to green, rapidly in solution and slowly in the solid state, possibly due to decomposition.

3.2. *IR spectra and structure simulations*

IR spectra of the complexes (table 1) show strong bands above 1460 cm^{-1} due to ν(C–N), indicating considerable double bond character in the C=N bonds [12, 13]. Positions of the $\nu(\mathrm{N}\overset{\cdots}{-}\mathrm{C})$ and ν(C–S) bands [14] clearly established the bidentate chelating mode of the ligands. Since suitable single crystals could not be grown for X-ray analysis

Table 1. Characteristic IR and ^{1}H NMR spectral data for the complexes.

		IR (cm^{-1})				^{1}H NMR (0 ppm) (23°C)	
		ν(C–N)	ν(N–C)	ν(C–S)	ν(M–S)	Me	C*H*
1	$V(S_2CNMe_2)_3$	1464	1147	972	438, 419		
2	$V(S_2CN^iPr_2)_3$	1491	1148	963	442, 421	1.5	4.3–4.9

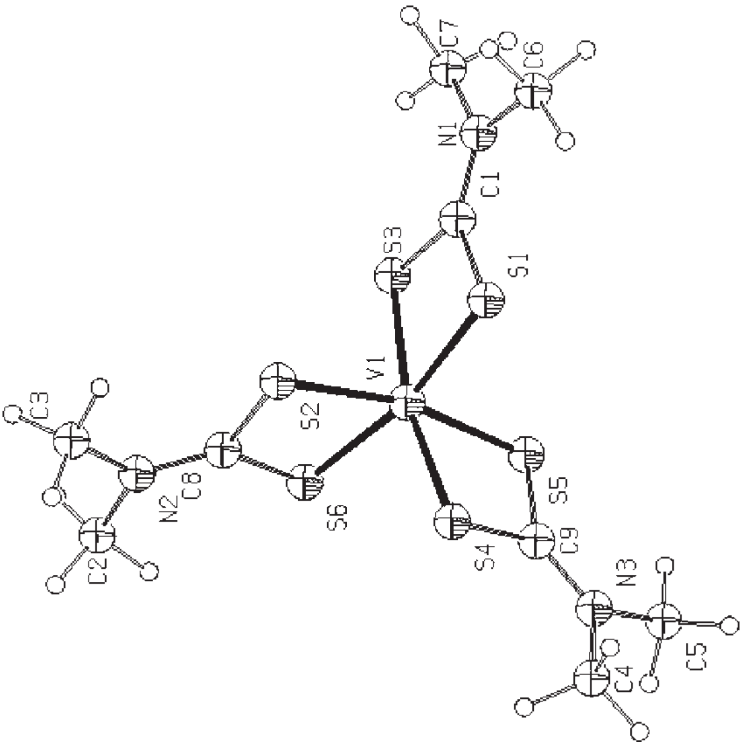

Figure 1. Simulated structure of complex **1**.

the molecular structure was simulated by performing molecular mechanics calculations using a modified version of Allinger's MM2 force-field [15]. The major additions to Allinger's force-field are a charge-dipole interaction term, a quartic stretching term, torsional and non-bonded constrains and automatic π-system calculations, whenever needed.

The simulated structure of **1** (figure 1) reveals that there is considerable π electron delocalization in the chelate rings; the mean S–C bond length, 1.79 Å, is shorter than the sum of C–S single bond covalent radii (1.81 Å). The average C=N distance of 1.35 Å is rather closer to the double bond (C=N, 1.27 Å) than the single bond value (C–N, 1.47 Å) [16]. The average V–S bond length is 2.30 Å and the bite angles range from 75.9° to 76.3°, leading to a twisted molecular core rather than trigonal anti-prismatic geometry. The best S_4V plane is constituted by S1, S3, S4, S5, V atoms. The mean deviation from the plane is 0.14 Å and the S2–V–S6 angle is 167.8°.

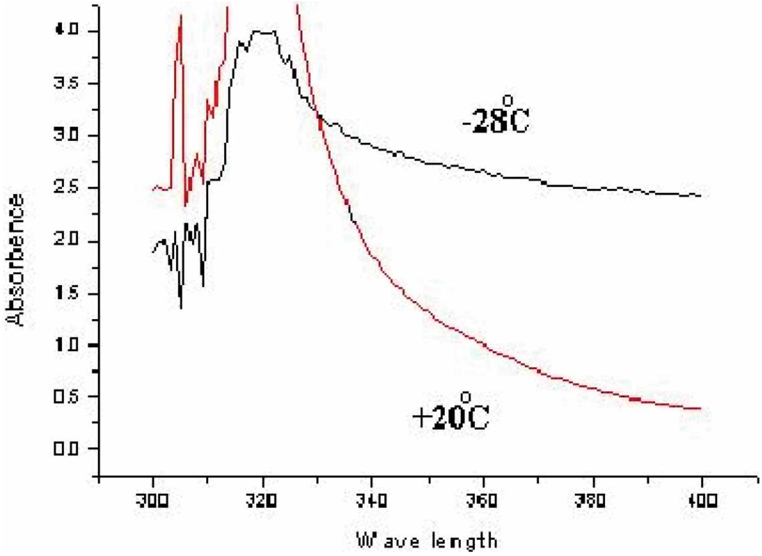

Figure 2. Absorption spectra of **1** in the UV region.

3.3. *Thermochromic charecteristics*

The complexes exhibit reversible thermochromism [17] in the solid state. On cooling (**1** below −28°C and **2** below −25°C), the colour of the complexes changes from yellow brown to light green. At room temperature the original colour is restored in a few minutes. The reversion to a yellow-brown colour was noticed even at −15°C. Thermochromism may be due to isomerization/deformation of the molecule or may be due to solid state effects. Electronic spectra of **1** in the solid state was recorded at different temperatures to monitor thermochromicity. It is evident from figure 2 that there are small but noticeable shifts in intraligand absorption bands (observed between 300 and 312 nm) when the temperature is lowered from room temperature to −28°C. Similarly, the high intensity charge transfer band is also affected by temperature variation. More conspicuous changes were observed in the visible region of the spectrum (figure 3). The room temperature spectrum shows two absorption bands at 632 and 745 nm, as is the case with many other octahedral V(III) complexes [18]. At −28°C, the absorption band at 745 nm vanishes and a new broad peak appears at 542 nm. It is noted that there is no observable change in the position of the peak at 632 nm.

Thermochromism is shown by a variety of compounds; a number of Schiff bases containing extensive π delocalized systems [4] are thermochromic. However, it is also possible to bring about a change in electronic spin state in a transition metal complex with small variations in temperature, resulting in a change of colour [19]. In the present case, the latter mechanism is not expected as there are only two electrons in the t_{2g} level and since the electrons are unpaired there is no question of a change in spin state. A change in π electron distribution in or outside the chelate ring or a rearrangement leading to a change in molecular geometry may also lead to thermochromism. However, in such cases the colour change will not be restricted to the solid state. Thus a possible explanation for the thermochromic behaviour could be formation

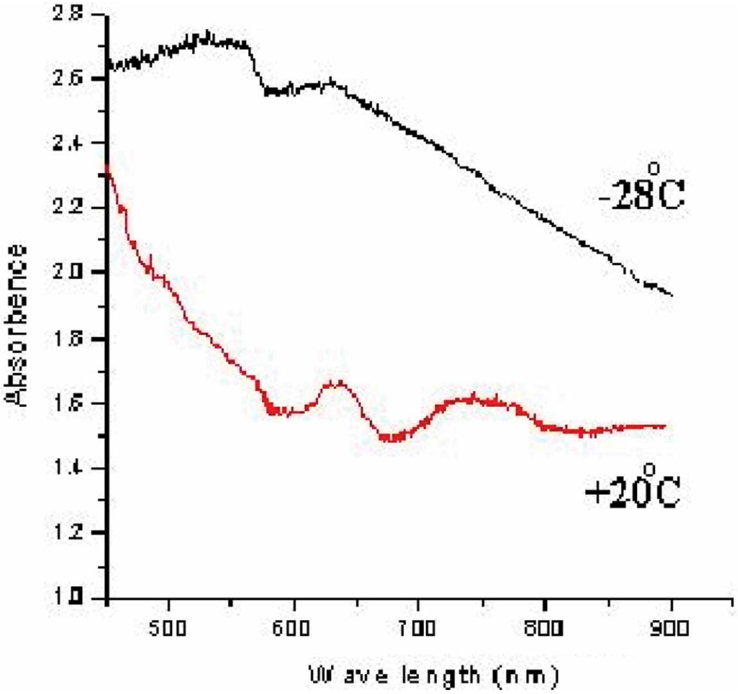

Figure 3. Absorption spectra of **1** in the visible region.

or dissociation of secondary bonds linking different molecules in the solid state arrangement of the molecules, as have been observed in tetraalkyldistibines and tetraalkyldibismuthines [20].

3.4. *Dynamic stereochemistry*

The ^{1}H NMR spectrum of **2** at +50°C shows signals due to methyl and methine protons (splitting is not very clear and the methine signal instead of a septet appears as a broad peak; figure 4). On cooling (below 23°C) the lines broaden to obscure spin coupling and a methyl singlet and a broad hump due to the methine protons are observed. Line broadening continues as the temperature is lowered further to −20°C (coalescence temperature), below which each of the signals splits into two. On further lowering of the temperature, the signals sharpen and at −61.6°C splitting of peaks due to methyl protons is visible. It was not possible to lower the temperature further for technical reasons. It is noted that the intensities of the two peaks are the same and the doublet observed at +50°C is the time averaged signal of the two.

Among various possible dynamic processes, the following three may lead to non-equivalence of isopropyl groups, resulting in such a signal pattern: (1) rotation about the $C\overset{\cdot\cdot}{=}N$ bond [21], (2) hindered rotation about N–C single bonds (in the N^iPr_2 units) [11] and (3) metal-centred rearrangement [22]. Molecular mechanics calculations performed on this complex show that the energy of $C\overset{\cdot\cdot}{=}N$ bond rotation is 158 kJ mol^{-1} and therefore this is a high temperature process. However, metal-centred

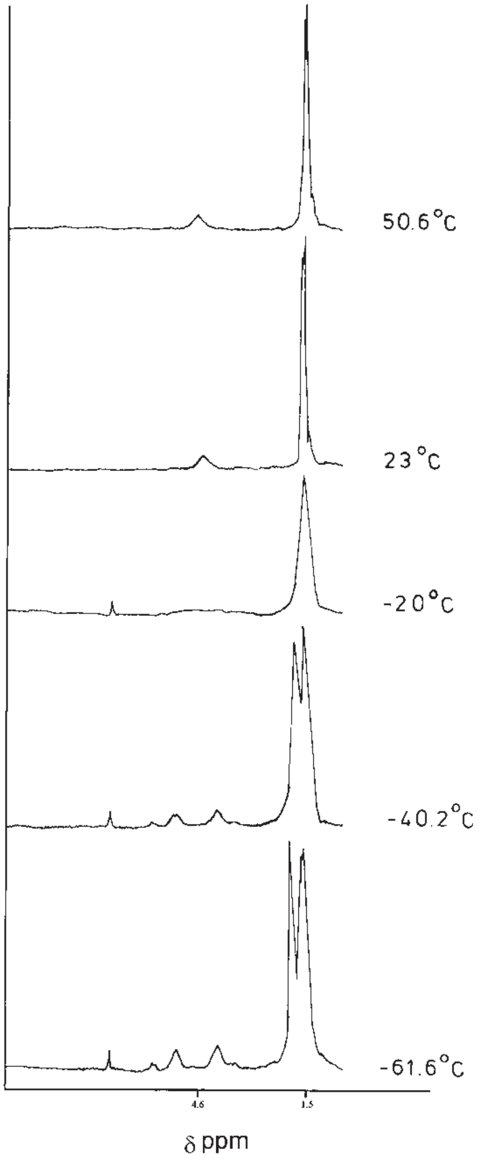

Figure 4. Variable temperature ^{1}H NMR spectra of **2**.

rearrangements are often very fast. Line broadening due to metal-centred isomerization in $V(S_2CN(Me)Ph)_3$ has been reported to start at −97°C [22].

The energy barrier for rotation about C–N single bonds in the N^iPr_2 units is obviously lower than that for a $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond and rotation about the former is hindered only at lower temperatures. Conventionally, the rate processes detected by variable temperature NMR are explained on the basis of line shape analysis. However, molecular mechanics calculations have been performed to find the energy barrier for the N–C bonds. The structure shown in figure 5(a) was the structure that was started with (which was found to be a local minimum), where both hydrogens are away

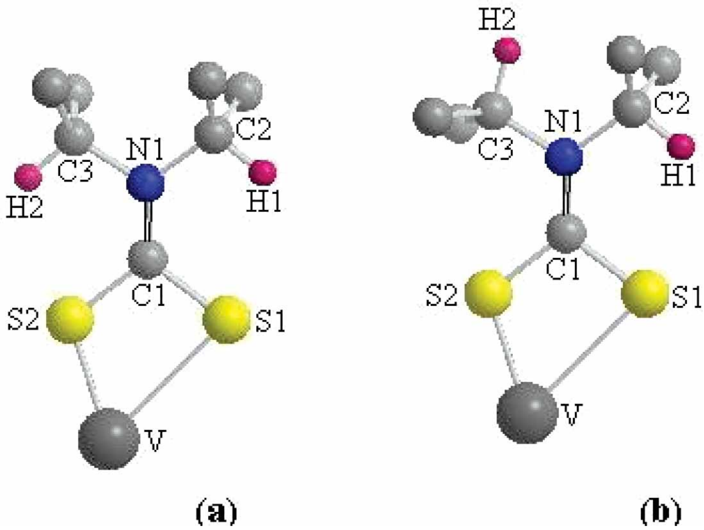

Figure 5. Structure of the V($S_2CN^iPr_2$) unit showing (a) local minimum and (b) global minimum conformations.

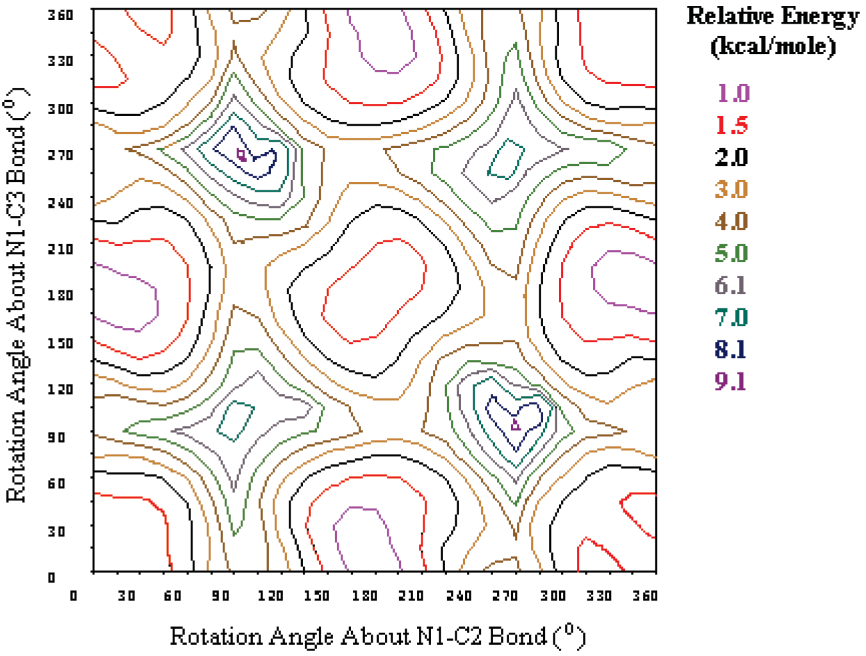

Figure 6. Contour map showing potential energy changes due to rotation of N–C bonds.

from each other and face towards the sulphur atoms, keeping the C1N1–C2H1 and C1N1–C3H2 interplanar angles at 0°. Then, each of the C–N bonds was rotated with a step size of 15° and the potential energy for each step calculated. Potential energy rises as one or both the C–N bonds are rotated and maxima are reached when two methyl groups from the two isopropyl units face each other. On further rotation the energy again decreases and another local minimum is reached when both the methine hydrogens become coplanar (both CN–CH dihedral angles are 180°). In the lowest energy structure the methine hydrogen of one isopropyl group faces the sulphur atom while that of the other isopropyl group though being coplanar is directed away from the sulphur atom. Thus the C1N1–C2–H1 and C1N1–C3H2 dihedral angles of the two isopropyl units are 0° and 180° (figure 5b). Change in potential energy as a function of rotation of the two N–C bonds in the ligand is shown in the contour diagram (figure 6). The energy barrier for this rotation is $38\,\mathrm{kJ\,mol^{-1}}$, which is comparable to those found in the case of Ti(IV) dithiocarbamates [11]. NMR splitting below $-20^{\circ}\mathrm{C}$ is thus due to hindered rotation about the C–N single bonds in the NC_2 moieties of the ligand framework. Kinetics of such C–N single bond, hindered rotations in dithiocarbamates has been reported [23].

Acknowledgement

The authors are grateful to Professor V.D. Gupta, Department of Chemistry, Banaras Hindu University, India, for his suggestions and for providing some of the chemicals.

References

[1] D. Coucouvanis. *Prog. Inorg. Chem.*, **26**, 301 (1979).
[2] S. Bhattacharya, N. Seth, D.K. Srivastava, V.D. Gupta, H. Noth, M. Thomann-Albach. *J. Chem. Soc., Dalton Trans.*, 2815 (1996).
[3] P. Hobza, H.L. Seizle, E.W. Schlag. *J. Am. Chem. Soc.*, **116**, 3500 (1994).
[4] L. Mishra, K. Bindu, S. Bhattacharya. *Indian J. Chem.*, **43A**, 317 (2004), and references therein.
[5] T. Shibahara, N. Iwai, M. Sasai, G. Sakane. *Chem. Lett.*, 445 (1997).
[6] D.C. Bradley, I.F. Rendall, K.D. Sales. *J. Chem. Soc., Dalton Trans.*, 2228 (1973).
[7] L. Que Jr, L.H. Pignolet. *Inorg. Chem.*, **2**, 351 (1974).
[8] L.F. Larkworthy, M.N. O'Donoghue. *Inorg. Chim. Acta*, **74**, 155 (1983).
[9] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann. *Advanced Inorganic Chemistry*, 6th edn, p. 722, John Wiley, New York (1999).
[10] R. Golding, P.C. Healy, P.W.G. Newman, E. Sinn, A.H. White. *Inorg. Chem.*, **11**, 2435 (1972).
[11] A.N. Bhatt, R.C. Fay, D.F. Lewis, A.F. Lindmark, S.H. Struass. *Inorg Chem.*, **13**, 886 (1974).
[12] R.D. Bereman, D. Nalewajek. *Inorg Chem.*, **16**, 2687 (1977).
[13] A.G. ElAmma, R.S. Drago. *Inorg. Chem.*, **16**, 2975 (1977).
[14] S. Bhattacharya, N. Seth, V.D. Gupta, H. Nöth, M. Thomann. *Z. Naturforsch.*, **49b**, 193 (1994).
[15] M.J. Duke, J.W. Ponder. *J. Comput. Chem.*, **16**, 791 (1995).
[16] J.A. Dean. *Lenges Handbook of Chemistry*, 13th edn, McGraw Hill, New York (1972).
[17] B. Munn. Molecular electronics, in *The New Chemistry*, N. Hall (Ed.), p. 401, Cambridge University Press, Cambridge (2000).
[18] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd edn, Elsevier, Amsterdam (1984).
[19] G. Wulfsberg. *Inorganic Chemistry*, p. 826, University Science Books, Sausalito, CA (2000).
[20] L.L. Lohr, A.J. Ashe III. *Organometallics*, **12**, 343 (1993), and references therein.
[21] B.L. Edgar, D.J. Duffy, M.C. Palazzotto, L.H. Pignolet. *J. Am. Chem. Soc.*, **95**, 1125 (1973).
[22] L. Que Jr, L.H. Pignolet. *Inorg. Chem.*, **13**, 315 (1974).
[23] A.F. Lindmark, R.C. Fay. *Inorg. Chem.*, **22**, 2000 (1983).