Molecular structure of monomeric scandium trichloride by gas electron diffraction and density functional theory calculations on ScCl$_3$ and Sc$_2$Cl$_6$ †

Arne Haaland,*,[a] Kjell-Gunnar Martinsen,[a] Dmitry J. Shorokhov,[a] Georgiy V. Girichev *,[b] and Vasili I. Sokolov[b]

[a] *Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway*
[b] *Department of Physics, State Academy of Chemistry and Technology, Engels 7, 153460 Ivanovo, Russia*

The molecular structures of monomeric and dimeric scandium trichloride were optimised by DFT calculations with basis sets of valence shell TZ + P quality, and the molecular force fields and normal vibrational modes calculated. Optimisation of ScCl$_3$ yielded an equilibrium geometry of D_{3h} symmetry and bond distance Sc–Cl 228.5 pm. Optimisation of a model of the dimer with double Cl bridges indicated an equilibrium geometry of D_{2h} symmetry, the terminal and bridging bond distances Sc–Cl$_t$ 226.0 and Sc–Cl$_b$ 247.5 pm, and the valence angles Cl$_t$–Sc–Cl$_t$ 114.9 and Cl$_b$–Sc–Cl$_b$ 86.6°. Synchronous gas electron diffraction (GED) and mass spectrometric (MS) data were recorded with the effusion cell kept at 900 ± 10 K. The gas was found to consist of 92 ± 2% monomer and 8 ± 2% dimer. Least-squares refinement of a trigonal pyramidal (C_{3v}) model of the monomer yielded the bond distance r_g(Sc–Cl) = 229.1(3) pm and a valence angle α Cl–Sc–Cl 119.8(5)°. The concentration of the dimer was too low for the GED data to give accurate structure parameters for this species. Bond energies for both monomer and dimer were calculated from thermochemical data in the literature and compared to corresponding energies in MCl$_3$ and M$_2$Cl$_6$, M = Al, Ga or In.

The monomeric scandium trihalides, ScX$_3$, have been the subject of several studies aiming towards the establishment of the molecular structure, *i.e.* the determination of the Sc–X bond distance and the molecular shape; is the equilibrium geometry trigonal pyramidal, symmetry C_{3v}, or planar, symmetry D_{3h}?

The first investigation of ScF$_3$ by gas electron diffraction (GED) dates back to 1961.[1] Diffraction data recorded at an unspecified temperature were found to be consistent with a monomer concentration of 100% and D_{3h} symmetry. This, of course, is the symmetry indicated by a spherical ion model, by the VSEPR model. It is also consistent with a hybridisation model since sd^2 hybrid orbitals formed from the 4s, 3d$_{xy}$ and 3d$_{x^2-y^2}$ atomic orbitals on Sc have major lobes pointing in the appropriate directions. (Hybridisation of the 4s, 3d$_{xz}$ and 3d$_{yz}$ orbitals would, however, yield hybrids favorable for a trigonal pyramidal co-ordination geometry.) Three reports on the IR absorption spectra of ScF$_3$ in rare gas matrices were published in the 60s or early 70s.[2–4] Since the symmetric Sc–F stretching frequency (ν$_1$) could not be found, it was concluded that the molecule must be planar or near-planar. The electric deflection of molecular beams, on the other hand, indicated a polar, *i.e.* non-planar structure,[5] and a second investigation by GED yielded a F–Sc–F valence angle of 110(2.5)°.[6]

Finally a third, careful analysis of GED data recorded with a nozzle temperature of 1750 K yielded a Sc–F bond distance of r_g = 184.7(2) pm and a non-bonded F···F distance which, after correction for thermal vibration, differed from that calculated for a planar model by 0.0(15) pm;[7] the molecule is clearly planar or very nearly so. Equilibrium geometries of D_{3h}

symmetry are also indicated by *ab initio* calculations at the CISD(Q) level[8] and by DFT calculations at the same level as those described below for ScCl$_3$.[9] It would seem that the question about the equilibrium structure of ScF$_3$ has been settled for the time being!

The gas-phase IR spectra of monomeric ScCl$_3$, ScBr$_3$ and ScI$_3$ have been recorded by Selivanov.[10] No symmetric Sc–X stretching frequencies (ν$_1$) could be assigned. The IR spectrum of matrix-isolated ScBr$_3$ has also been reported; ν$_2$, ν$_3$ and ν$_4$ could be assigned, but ν$_1$ was not found.[11] Neither the trichloride nor the tribromide appears to have been studied by GED up to the present, but Ezhov *et al.*[12] have recently published the results of a GED study of gaseous ScI$_3$ at 1050 K. The molecular beam was found to contain both monomeric and dimeric species with mole fractions of 21(3) and 79(3)% respectively. Least-squares refinement of the molecular structures of both monomer and dimer yielded a monomer bond distance of 262(1) pm and a monomer valence angle of 117(2)°: the concentration of the monomer is obviously too small to allow a distinction to be made between planar and pyramidal models.

In this article we report the results of density functional theory (DFT) calculations on both monomeric and dimeric scandium trichloride and a GED investigation which shows that monomeric ScCl$_3$ is trigonal planar or very nearly so.

Density Functional Theory Calculations

The original plan was to optimise the molecular structures of both ScCl$_3$ and Sc$_2$Cl$_6$ by DFT calculations using the program system GAUSSIAN 94[13] with the Becke exchange[14] and the Perdew–Wang correlation functional[15] (BPW 91). Optimisation of a trigonal planar (D_{3h}) model of ScCl$_3$ with the standard effective core potential (ECP) basis LanL2DZ[13] converged to a bond distance of 229.1 pm. The dimer was assumed to have a diborane-like structure with two bridging chlorine atoms (see

---

Table 1 Structure parameters of $ScCl_3$ and Sc_2Cl_6 obtained by density functional theory calculations or gas electron diffraction. Interatomic distances (r), root-mean-square vibrational amplitudes (l), perpendicular amplitude correction coefficients (K) and shrinkages (δ) in pm, angles in °[a]

	DFT[b]			GED	
	r_e	l	K	r_g	l
$ScCl_3$				Mole fraction 93(3)%	
Interatomic distances					
Sc–Cl	228.5	7.8	3.6	229.1(3)	7.6(2)[d]
Cl···Cl	395.7	23.6	0.6	390.8(11)	23.3(10)[d]
Shrinkage					
δ(Cl···Cl)[c]	6.1			6.0(16)	
Valence angle	e			α	
Cl–Sc–Cl	120.0			119.8(5)	
Sc_2Cl_6				Mole fraction 7(3)%	
Interatomic distances					
Sc–Cl$_t$	226.0	7.7	27.6	227.5(10)[d]	7.6(2)[d]
Sc–Cl$_b$	247.5	11.7	8.8	246(2)	[11]
Cl$_b$···Cl$_b$	339.5	15.5	3.5	325(6)	[15.5]
Sc···Sc	360.1	14.0	2.1	349(4)	[14.0]
Cl$_b$···Cl$_t$	394.9	37.2	26.0	404(2)	37.6(10)[d]
Cl$_t$···Cl$_t$	380.4	25.5	42.4	412(2)	[25.5]
Sc···Cl$_t$	517.8	64.4	8.3	501(3)	[45.0][d]
Cl$_t$···Cl$_t$	603.0	165.2	4.3	543(3)	[51.0][d]
Cl$_t$···Cl$_t$	713.1	39.0	1.1	691(3)	[39]
Valence angles	e			α	
Cl$_t$–Sc–Cl$_t$	114.9			[114.9]	
Cl$_b$–Sc–Cl$_b$	86.6			86(2)	
Sc–Cl$_b$–Sc	93.4			94(2)	
R factor[e]				0.053	

[a] Estimated standard deviations in parentheses in units of the last digit. Non-refined parameters in square brackets. [b] The calculations on $ScCl_3$ have been carried out with the ADF program and the TZ + P basis set IV, that on Sc_2Cl_6 with GAUSSIAN 94 and a 6-311G* basis set. See comment in Density Functional Theory Calculations. [c] The shrinkage is defined as δ(Cl···Cl) = $\sqrt{3}$ r_g(Sc–Cl) − r_g(Cl···Cl). [d] See comment in Structure refinements. [e] $\sqrt{[\Sigma w(I_{obs} − I_{calc})^2/\Sigma w(I_{obs})^2]}$.

sketch in Contents). Optimisation of a model of D_{2h} symmetry with the LanL2DZ basis yielded the terminal and bridging bond distances Sc–C$_t$ 227.5 and Sc–Cl$_b$ 251.2 pm.

Optimisation of a C_{2v} model of the dimer (*i.e.* a model in which the central Sc_2Cl_2 ring is non-planar) with the standard all-electron (AE) basis set 6-311G*[13] converged to D_{2h} symmetry (planar Sc_2Cl_2 ring). Interatomic distances and valence angles are listed in Table 1. The normal vibrational modes are listed in Table 2. The molecular force field was transferred to the program ASYM 40 for calculation of root-mean-square vibrational amplitudes, l, and perpendicular amplitude correction coefficients K[16] (see Table 1).

After several attempts to optimise the structure of the monomer at the BPW91/6-311G* level had failed to converge, we turned to the Amsterdam Density Functional (ADF) program.[17] Calculations were carried out with the Vosko–Wilk–Nusair parametrisation,[18] the gradient correction of Becke[14] for exchange and of Perdew[19] for correlation. A standard basis set of TZ + P quality (IV) was used,[17] with the atomic cores of Sc and Cl up to and including the 2p AOs frozen in their atomic shape. Structure optimisation of a C_{3v} model of $ScCl_3$ now converged nicely to yield a structure of D_{3h} symmetry. The vibrational modes are listed in Table 2, the bond distance, root mean square (r.m.s.) vibrational amplitudes and perpendicular amplitude correction coefficients are listed in Table 1.

Experimental

A sample of $ScCl_3 \cdot xH_2O$ with a stated purity of 99.99% was purchased from Aldrich Chemical Company. The anhydrous trichloride was obtained by heating the sample under reflux with thionyl chloride as described in ref. 20.

Table 2 Normal mode frequencies (cm^{-1}) of $ScCl_3$ and Sc_2Cl_6 obtained by DFT calculations

Symmetry	Mode	ω	Symmetry	Mode	ω
$ScCl_3$ (D_{3h})					
A_1	1	341	E	2	468
E	3	86	A_2	4	79
Sc_2Cl_6 (D_{2h})					
A_g	1	438	A_g	2	287
A_g	3	151	A_g	4	71
B_{1g}	5	237	B_{1g}	6	81
B_{2g}	7	465	B_{2g}	8	58
B_{3g}	9	73	A_u	10	36
B_{1u}	11	474	B_{1u}	12	109
B_{1u}	13	12	B_{2u}	14	319
B_{2u}	15	56	B_{3u}	16	412
B_{3u}	17	273	B_{3u}	18	94

Gas electron diffraction and mass spectrometry

Synchronous MS and GED experiments were carried out on the modified EMR-100/ApdM-1 unit in Ivanovo. The nickel oven containing the sample was kept at the lowest possible temperature at which sufficient vaporisation took place, about 900 K, corresponding to a vapour pressure of about 0.025 Torr (Torr ≈ 133 Pa).[21] The ratio of evaporation surface to the nozzle orifice was approximately 400. The length to diameter ratio of the diffusion nozzle was optimised to keep equilibrium concentrations of the monomer and dimer in the vapor and a negligibly small scattering volume.[22] Other experimental
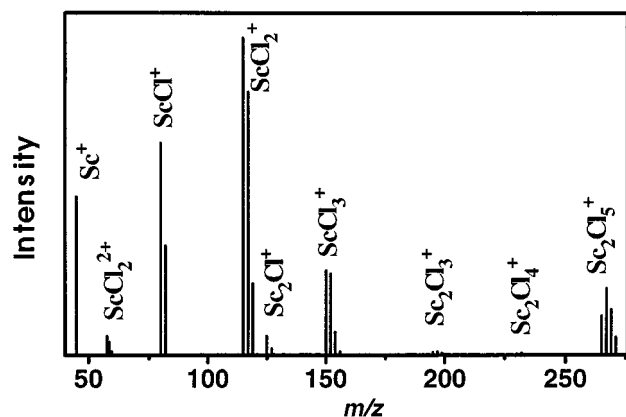
Fig. 1 A portion of the mass spectrum of scandium trichloride under the conditions of the gas electron diffraction experiment. The ionising potential is 50 V
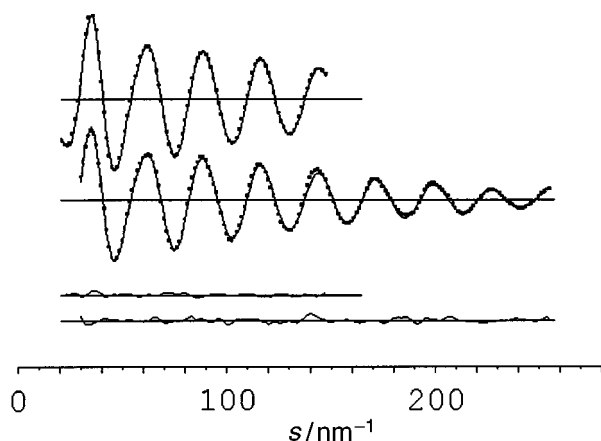

Fig. 2 Calculated (full lines) and experimental (squares) modified molecular intensity curves of $ScCl_3$ with difference curves shown below
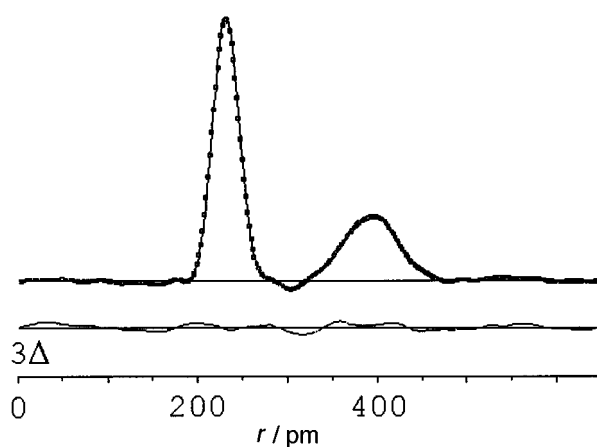

Fig. 3 Calculated (full line) and experimental (squares) radial distribution curves of a mixture of $ScCl_3$ (92%) and Sc_2Cl_6 (8%). Artificial damping constant $k = 25$ pm². The two peaks at about 230 and 390 pm represent the Sc–Cl bond distance and the non-bonded Cl···Cl distance in the monomer. Below: difference curve

conditions are summarised in SUP 57406. A portion of the mass spectrum is given in Fig. 1. For analysis of the gas composition we assumed that the ions $ScCl_n^+$, $n = 1$ to 3, are formed from the monomer, that the ions $Sc_2Cl_n^+$, $n = 1$ to 5, are formed from the dimer, and that the ratio of the ionisation cross-sections of dimer to monomer is equal to 2.

Atomic electron scattering factors were taken from ref. 23 and backgrounds were drawn as smooth least-squares adjusted polynomials to the difference between experimental and calculated molecular intensities.

Structure refinements

Structure refinement of the monomer was based on a geometrically consistent r_a model of C_{3v} symmetry. The mole fraction of monomer in the molecular beam, the Sc–Cl bond distance, the non-bonded Cl···Cl distance and the Sc–Cl and Cl···Cl r.m.s. vibrational amplitudes were refined as independent parameters. The asymmetry constant of the Sc–Cl bond distance (and of the terminal Sc–Cl distance in the dimer) was estimated from $\kappa = (1/6)l^4\sqrt{[8\pi^2c\omega_e x_e\mu/h]}$. Molecular constants taken from the scandium monochloride molecule[24] yielded $\kappa = 7.24 \times 10^{-6}$ pm³.

Structure refinement of the dimer was based on a geometrically consistent r_a model of D_{2h} symmetry. Such a model is characterised by four independent structure parameters, *e.g.* the terminal and bridging Sc–Cl$_t$ and Sc–Cl$_b$ bond distances and the valence angles α Cl$_t$–Sc–Cl$_t$ and Cl$_b$–Sc–Cl$_b$. Since the amount of dimer in the molecular beam was less than 10% we were unable to refine these four parameters without divergence, and the valence angle α Cl$_t$–Sc–Cl$_t$ was fixed at the value obtained by the DFT calculations. The difference between the

Sc–Cl bond distance in the monomer and the terminal distance in the dimer, $r_g(Sc–Cl) - r_g(Sc–Cl_t)$, was fixed at the value obtained by DFT calculations with LanL2DZ basis (1.6 pm). (The estimated standard deviation obtained for the Sc–C$_t$ bond distance was expanded from 0.3 to 1.0 pm to include the uncertainty due to this constraint.) The vibrational amplitudes of the two bond distances were refined with a constant difference, as were the amplitudes of the Cl···Cl distance in the monomer and of the Cl$_b$···Cl$_t$ distance in the dimer which turned out to be very similar. The calculated vibrational amplitudes of the non-bonded Sc···Cl$_t$ distance at about 500 pm and the non-bonded Cl$_t$···Cl$_t$ distance at about 540 pm were 64 and 165 pm respectively. These amplitudes were varied stepwise to minimise the square-error sum. The best fit was obtained for the values 45 and 51 pm respectively. Other amplitudes were fixed at their calculated values.

The structures were refined by a modified version of the program KCED 25 originally written by H. M. Seip. The refinements converged to yield the best values listed in Table 1. Since the refinements were carried out with diagonal weight matrices the listed estimated standard deviations have been multiplied by a factor of 2.0 to include the uncertainty due to data correlation and expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated molecular intensity curves are compared in Fig. 2, radial distribution curves in Fig. 3.

Results and Discussion

The composition of the molecular beam

The mass spectra recorded simultaneously with the GED diagrams indicated that the mole fractions of monomers and dimers in the molecular beam were 92 ± 2 and $8 \pm 2\%$ respectively, while the amount of trimer or higher species was negligible. These mole fractions are in good agreement with the less accurate values obtained by analysis of the electron diffraction data, 93(3) and 7(3)% respectively. The high concentration of the monomer allows an accurate determination of its molecular structure, while the concentration of the dimer was too low for the GED diagrams to contain much information about the molecular structure of Sc_2Cl_6.

The molecular structure of $ScCl_3$

Least-squares structure refinement of a molecular model of C_{3v} symmetry to the GED data yielded a Cl–Sc–Cl valence angle

of 119.8(5)° while structure optimisation by DFT calculations with an all-electron basis of TZ + P quality yielded an equilibrium structure of D_{3h} symmetry; calculations and experiment agree that the molecule is planar or very nearly so. A planar equilibrium structure is also indicated by the gas phase IR spectra since the symmetric Sc–Cl stretching mode (ν_1) could not be detected.[10] The calculated Sc–Cl bond distance is 228.5 pm in good agreement with experimental (r_g) distance of 229.1(3) pm.

Before going on to discuss the molecular structures of the monomeric trichlorides of the heavier Group 3 metals, yttrium and lanthanum, we pause to note that while the bond distances in the Group 13 trichlorides MCl$_3$, M = Al, Ga or In, are 6 to 11 pm shorter than the bond distance in the monochlorides MCl,[25] the bond distance in ScCl$_3$ is 6 pm *longer* than in ScCl, 222.9 pm.[26]

An early GED investigation of YCl$_3$ indicated that the equilibrium structure is planar.[27] More recently, Konings and Booij[28] have recorded the infrared spectrum of gaseous YCl$_3$ and assigned the four normal modes under the assumption that the structure is pyramidal. This assignment has been challenged by Marsden and Smart[29] who optimised the structure at the MP2 level with a ECP basis of DZ quality and obtained an equilibrium structure of D_{3h} symmetry. Finally, a reinvestigation by a combination of GED and DFT calculations has shown that the structure is indeed planar or very nearly so.[30]

The equilibrium structure of monomeric LaCl$_3$ is still not definitely established. Two relatively recent investigations of LaCl$_3$ by GED led to the conclusion that the equilibrium geometry is pyramidal,[31,32] while quantum chemical calculations at various levels indicate that it is planar.[33–36]

The molecular structure of Sc$_2$Cl$_6$

Density functional theory calculations on the dimer with a 6-311G* basis converged to a model of D_{2h} symmetry. Bond distances and valence angles are listed in Table 1.

Attempts to refine the four independent structure parameters characterising a D_{2h} model, *viz.* the terminal and bridging Sc–Cl$_t$ and Sc–Cl$_b$ bond distances and the valence angles α Cl$_t$–Sc–Cl$_t$ and Cl$_b$–Sc–Cl$_b$, to the GED data failed to converge. The difference between the Sc–Cl bond distance in the monomer and the terminal distance in the dimer, r_g(Sc–Cl) − r_g(Sc–Cl$_t$), was therefore fixed at the value obtained by DFT calculations with LanL2DZ basis (1.6 pm), and Cl$_t$–Sc–Cl$_t$ at the value obtained by the all-electron calculations on the dimer. The best values obtained for the two structure parameters that could be refined without constraints r_b(Sc–Cl$_b$) = 246(2) pm and α Cl$_b$–Sc–Cl$_b$ 86(2)° are not significantly different from their calculated values. In the following we base our discussion of the dimer on the calculated structure parameters.

The compound Sc$_2$Cl$_6$ appears to be similar to the Group 13 analogues M$_2$Cl$_6$, M = Al,[37] Ga[37,38] or In,[38] insofar as the bridging M–Cl distance is about 20 pm longer than the terminal and the Cl$_b$–Sc–Cl$_b$ angle is close to 90°, but to differ from the Group 13 analogues by having a Cl$_t$–Sc–Cl$_t$ less than 120°: Cl$_t$–Al–Cl$_t$ 123.6(16),[37] Cl$_t$–Ga–Cl$_t$ 124.7(18)[37] and Cl$_t$–In–Cl$_t$ ≈ 130°.[38]

The crystal structure of ScCl$_3$ is constructed from ScCl$_6$ octahedra, each Cl atom bridges two Sc atoms at a distance, 252 pm, about 5 pm longer than the Sc–Cl$_b$ distance in the gaseous dimer.[39]

Bond energies

The mean bond energy of monomeric ScCl$_3$ at 298 K may be calculated from the standard enthalpy of formation:[24] MBE(ScCl$_3$) = {ΔH°_f[Sc(g)] + 3ΔH°_f[Cl(g)] − ΔH°_f[ScCl$_3$(g)]}/3 = 478(3) kJ mol^{-1}. Similarly the mean bond energy of gaseous LaCl$_3$ calculated from the standard enthalpy of formation[40] is

found to be 509 kJ mol^{-1}. Both the Sc–Cl and La–Cl MBEs are larger than those of the Group 13 analogues, MCl$_3$, M = B, Al, Ga or In, which range from 456 to 327 kJ mol^{-1}.[25] While the MBEs of the Group 13 trichlorides decrease as the group is descended, those of the Group 3 trichlorides appear to increase.

Since the terminal Sc–Cl bond distance in Sc$_2$Cl$_6$ is very close to the bond distance of the monomer, we assume the bond energies to be equal; BE(Sc–Cl$_t$) = MBE(ScCl$_3$). The mean energy of the bridge bonds may then be estimated from the dimerisation enthalpy,[41] ΔH°_d = −199 kJ mol^{-1} where ΔH°_d = 2 BE(Sc–Cl$_t$) − 4 BE(Sc–Cl$_b$) or BE(Sc–Cl$_b$) = 289 kJ mol^{-1}. The M–Cl$_b$ bond is thus stronger in Sc$_2$Cl$_6$ than in Al$_2$Cl$_6$, Ga$_2$Cl$_6$ or In$_2$Cl$_6$.[38] The ratio between terminal and bridging bond energies is however 1.7 ± 0.1 for both Sc and the Group 13 metals.[38]

References

1 P. A. Akishin and V. A. Naumov, *J. Struct. Chem.*, 1961, **2**, 1.
2 D. McDonald, jun. and W. Weltner, jun., *J. Phys. Chem.*, 1966, **70**, 3293.
3 R. H. Hauge, J. W. Hastie and J. L. Margrave, *J. Less Common Met.*, 1971, **23**, 359.
4 J. W. Hastie, R. H. Hauge and J. L. Margrave, *J. Less Common Met.*, 1975, **39**, 309.
5 E. W. Kaiser, W. E. Falconer and W. Klemperer, *J. Chem. Phys.*, 1972, **56**, 5392.
6 N. I. Giricheva, E. Z. Zasorin, G. V. Girichev, K. S. Krasnov and V. P. Spiridonov, *J. Struct. Chem.*, 1976, **17**, 686.
7 E. Z. Zasorin, A. A. Ivanov, L. I. Ermolaeva and V. P. Spiridonov, *Zh. Fiz. Khim.*, 1989, **63**, 669.
8 V. G. Solomonik, V. V. Sliznev and N. B. Balabanov, *Zh. Neorg. Khim.*, 1995, **40**, 2024.
9 A. Haaland and K.-G. Martinsen, unpublished work.
10 G. K. Selivanov, Ph. D. Thesis, Moscow State University, 1972.
11 P. A. Perov, S. V. Nedyak and A. A. Maltsev, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1975, **16**, 281.
12 Yu. Ezhov, S. A. Komarov and V. G. Sevastyanov, *Zh. Strukt. Khim.*, 1997, **38**, 489.
13 GAUSSIAN 94, revision D.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Repogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
14 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
15 J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13 244.
16 L. Hedberg and I. M. Mills, *J. Mol. Spectrosc.*, 1993, **160**, 117.
17 Amsterdam Density Functional (ADF), Release 2.1.1, Vrije Universiteit, Amsterdam, 1995; E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41; E. J. Baerends, Ph. D. Thesis, Vrije Universiteit, Amsterdam, 1975; P. M. Boerigter, G. te Velde and E. J. Baerends, *Int. J. Quantum Chem.*, 1988, **33**, 87.
18 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
19 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
20 J. H. Freeman and M. L. Smith, *J. Inorg. Nucl. Chem.*, 1958, **7**, 224.
21 Yu. B. Patrikeev, V. A. Morozova, G. P. Dudchik, O. G. Polyachonok and G. I. Novikov, *Zh. Fiz. Khim.*, 1973, **47**, 266.
22 G. V. Girichev, S. A. Shlykov and S. B. Lapshina, *Zh. Fiz. Khim.*, 1990, **64**, 899.
23 R. A. Bonham and L. Schäfer, in *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

24 *Molecular Constants of Inorganic Compounds*, ed. K. S. Krasnov, Chemistry, Leningrad, 1977.
25 A. Haaland, A. Hammel, K.-G. Martinsen, J. Tremmel and H. V. Volden, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 2209.
26 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York, 1979, vol. IV.
27 P. A. Akishin, V. A. Naumov and V. M. Tatevskii, *Kristallografiya*, 1959, **4**, 194.
28 R. J. M. Konings and A. S. Booij, *J. Mol. Struct.*, 1992, **271**, 183.
29 C. J. Marsden and B. A. Smart, *Aust. J. Chem.*, 1993, **46**, 749.
30 J. Molnár, M. Kolonits, C. J. Marsden and M. Hargittai, manuscript in preparation.
31 T. G. Danilova, G. V. Girichev, N. I. Giricheva, K. S. Krasnov and E. Z. Zasorin, *Izv. Vyssh. Uchen. Zaved. Khim. Khim. Tekhnol.*, 1979, **22**, 101.
32 V. P. Spiridonov, A. G. Gershikov and V. S. Lyutsarev, *J. Mol. Struct.*, 1990, **221**, 79.
33 L. L. Lohr and Y. Q. Jia, *Inorg. Chim. Acta*, 1985, **119**, 95.
34 M. Dolg, H. Stoll and H. Preuss, *J. Mol. Struct.* (*THEOCHEM*), 1991, **235**, 67.
35 S. Di Bella, G. Lanza and I. L. Fragalà, *Chem. Phys. Lett.*, 1993, **214**, 598.
36 G. Lanza and I. L. Fragalà, *Chem. Phys. Lett.*, 1996, **255**, 341.
37 Q. Shen, Ph. D. Thesis, Oregon State University, Corvallis, 1974.
38 G. V. Girichev, N. I. Giricheva, V. A. Titov and T. P. Chusova, *J. Struct. Chem.*, 1992, **33**, 362.
39 H. Fjellvåg and P. Karen, *Acta Chem. Scand.*, 1994, **48**, 294.
40 I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim, 1993, Parts I and II.
41 K. Wagner and H. Schäfer, *Z. Anorg. Allg. Chem.*, 1977, **430**, 43.