Effective core potential DFT calculations of nuclear shielding as a tool for the prediction and assignment of the tungsten chemical shift in mono- and polynuclear complexes

Alessandro Bagno [*], Marcella Bonchio

Centro CNR Meccanismi Reazioni Organiche, Dipartimento di Chimica Organica, Università di Padova, via Marzolo 1, I-35131 Padova, Italy

Abstract

The shielding of the ^{183}W nucleus in mononuclear tungsten complexes and in the Keggin heteropolyoxotungstate $PW_{12}O_{40}^{3-}$ has been investigated by a density functional theory (DFT) method with effective core potentials. Calculated shieldings correlate with experimental data, although they are one order of magnitude lower than the experimental values, which is reflected in low slopes (< 0.1) of the correlation lines. The influence of molecular geometry (semi-empirical vs. DFT) on the nuclear shielding is examined. There is a fair correlation between atomic charges at W and nuclear shielding only for species sharing the same formal oxidation state. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The NMR observation of transition metal nuclei [1,2] provides a direct tool to investigate the structural and electronic properties of metal sites in a coordination environment, thus finding important applications in different research fields including biology, catalysis and material science.

The shielding of heavy nuclei, and especially of transition metals, is determined by the paramagnetic term σ^p, which depends on the mixing of excited states of appropriate energy and symmetry with the ground state in the presence of a magnetic field [1]. Owing to the availability of many such states, the shielding range of metal nuclei tends to be very wide ($10^3–10^4$ ppm), so that chemical shifts are extremely sensitive to even minor ligand changes [1,2]. The dependence of these chemical shifts on the structure of the metal complex is largely unpredictable, which hampers a straightforward assignment and even detection of the expected resonances. As a consequence, the NMR analysis of polynuclear species displaying several metal sites in non-equivalent environments poses a severe challenge [3].

The case of tungsten complexes is very indicative. A considerable body of experimental NMR chemical shifts is available for ^{183}W (14.4% nat. abundance, $I = 1/2$), spanning ca. 8000 ppm [1,2]. Despite its low sensitivity, the high resolution attainable in the NMR spectra of this nucleus renders it a convenient structural probe for the very large and complex species that this element can form. Thus, for example, Keggin-type heteropolytungstates with general

* Corresponding author. Fax: +39-498275239; e-mail: alex@chor.unipd.it

formula $MXW_{11}O_{39}^{q-}$ exhibit six distinct [183]W signals lying in a relatively narrow range (ca. 100 ppm), whose assignment is only based on empirical criteria, i.e., the relationship between $^2J_{WOW}$ scalar coupling constants and the W-O-W angle [3] or between chemical shift and charge density [4].

The ab initio calculation of nuclear shieldings provides an attractive method for structure elucidation, since it should yield an independent estimate of the chemical shift which can then (a) be used to predict the spectral region in which an NMR signal can be found, and (b) ultimately serve for spectral assignment through the comparison with experimental values. Various approaches have been adopted for the calculation of the shielding of various NMR-active nuclei; thus, besides the coupled Hartree–Fock (CHF) method, several methods (IGLO, LORG, GIAO or CSGT) have been developed for coping with the well-known problem of the invariance of the gauge origin of the vector potential. The latter calculations can be carried out within Hartree–Fock or density-functional theory [5–11]. Good correlations between calculated and experimental chemical shifts for ^{13}C and [15]N [12], ^{14}N and [17]O [13], and [33]S [14] have been found. Much emphasis has been placed on obtaining a near-unit slope in such correlations, which implies a correct prediction of the absolute magnitude of the nuclear shielding. Certain coupled-cluster [15] and DFT [16] benchmark calculations have been shown to attain chemical accuracy.

While there are several examples of calculations on first-row transition metal shifts [5–10,17–20], and of [17]O shifts in metal oxo complexes [21–23], such calculations on second- and third-row ones with all-electron basis sets become rapidly intractable even for moderately sized species, which is a major difficulty for polynuclear tungsten complexes. Moreover, the substantial relativistic effects on their energy and electronic structure [10] must be accounted for [24]. However, taking all such effects into account the tungsten chemical shift in the simple symmetric complex $W(CO)_6$ could be calculated satisfactorily [24].

A solution is provided by effective core potentials (ECPs), where core electrons up to a given shell are treated by means of pseudopotentials (which also incorporate some relativistic corrections) and only valence electrons are explicitly treated. Such an approach is based on the idea that chemical properties depend primarily on valence rather than core electrons, and considerably simplifies (or may indeed permit) the calculations. However, the molecular orbitals derived from ECPs have the correct shape only at distances from the nucleus larger than the core radius, whereas at shorter distances they decrease monotonically to zero [24,25]. This causes a difficulty with shielding calculations, because σ^p is calculated by means of integrals containing a r^{-3} dependence, which are very sensitive to the behavior of MOs near the nucleus, i.e., where they have very small values. As a consequence, σ^p values thus calculated are underestimated by several orders of magnitude [25]. However, if this underestimation is consistent for the nuclei in different chemical species the results may still provide the correct ordering of chemical shifts. Therefore, if a correlation between calculated and experimental values is found, after calibration with known chemical shifts such an approach will still be operationally valid, and yield calculated shifts for the purposes listed above.

These issues have partly been addressed by a study where [49]Ti shieldings in titanium halides calculated with all-electron and ECP basis sets have been compared [26]. It was found that the contribution from 1s, 2s and 2p shells is large but entirely diamagnetic and essentially constant, and the contribution from the outermost core electrons (3s and 3p) is smaller, paramagnetic and considerably variable.

Since the ECP model chemistry is currently the only practical one for the study of heavy atoms, it is of interest to ascertain whether it can provide the correct chemical shift trend. To this effect, we have undertaken a computational study of the nuclear shielding in tungsten compounds for which experimental data were available. All calculations were carried out with GAUSSIAN 98 [27] and SPARTAN 5.0 [28].

2. Results and discussion

2.1. [183]W shielding

Among available ECPs, those by Hay and Wadt (LANL) [29], Stevens et al. (CEP) [30] and Dolg and co-workers (SDD) [31] have come into common use.

Basis sets for use with these ECPs are built by fitting the ECP to Gaussian functions according to various schemes. Apart from the differences in their definition, they also differ in the way light atoms and valence electrons are treated. (a) In the case of LANL and SDD, first-row atoms are treated with all-electron basis sets (D95 and D95V, respectively), whereas first-row atoms are also treated by means of ECPs in the case of CEP. (b) In the case of LANL, electrons in the valence and the outermost closed shells are explicitly treated with a basis set of double-zeta quality (D95; this combination was designed for species having few or none formal valence electrons, like W^{VI}). (c) CEP basis sets differ according to the contraction scheme; in this work we employed the basis set with a triple-split contraction. Hereafter,

the basis sets derived from the above ECPs will be referred to as LANL2DZ, CEP-121G and SDD, respectively.

All calculations were carried out at a DFT level (Becke's hybrid 3-parameter functional with Lee–Yang–Parr correlation, B3LYP) [20].

The geometry was optimized both at the semi-empirical PM3(tm) [28] and at the DFT level (using a (99 302) integration grid). Nuclear shieldings were calculated with the GIAO method [10]. For two species (WO_4^{2-} and WS_4^{2-}), which share the same formal valence state and symmetry but have very different chemical shifts, the calculations were run also by means of the CSGT method [10] and with LANL2DZ, CEP-121G and SDD at the LANL2DZ geometry (Table 1).

Table 1
Calculated and experimental NMR parameters of ^{183}W in tungsten complexes

Species	LANL2DZ						$q(W)$		CEP-121G			Exptl δ^d
	PM3(tm)^a			LANL2DZ^b			NBO	ChelpG^h	CEP-121G^c			
	σ^e	$\Delta\sigma^f$	calcd. δ^g	σ^e	$\Delta\sigma^f$	calcd. δ^g			σ^e	$\Delta\sigma^f$	calcd. δ^g	
W^0 species												
$W(\eta-C_5H_5)_2H_2$	48.4	20.6	-255	37.3	23.8	-208	0.163	0.304	27.0	24.6	-211	-4670 [34]
$W(CO)_6$	29.9	0	-237	37.8	0	-208	-0.739	-3.239	18.7	0	-203	-3446 [1]
W^{VI} species												
WF_6	-156.5	0	-50	-145.6	0	-25	2.573	2.163	-153.3	0	-31	-1120 [34]
WF_5OMe	-165.9	22.4	-41	-131.5	1.7	-39	2.509	2.024	-136.7	0.45	-47	-1068 [34]
WF_5O^-	-174.5	83.6	-32	-162.4	83.2	-8	2.384	2.150	-169.9	87.2	-14	-504 [34]
$WO_3 (C_{3v})$	-271.0	62.2	64	-234.7	70.9	64	1.997	1.806	-249.9	81.4	66	-280 [34]
WO_4^{2-}	-206.7^i	0	0	-170.6^j	0	0	2.029	1.489	-184.2^k	0	0	0 [1,34]
WO_3S^{2-}	-228.9	67.8	22	-201.7	51.8	31	1.721	1.173	-216.4	55.5	32	841 [35]
$WO_2S_2^{2-}$	-262.7	74.7	56	-243.6	76.5	73	1.313	0.939	-260.7	81.0	76	1787 [35]
WCl_6	-226.9	0	20	-337.3	0.032	167	0.323	0.648	-340.2	0	156	2182 [34]
WOS_3^{2-}	-300.2	50.0	93	-293.9	57.2	123	0.819	0.782	-314.9	61.9	131	2760 [35]
WS_4^{2-}	-340.7	0	134	-351.7^l	0	181	0.252	0.640	-378.1	0	194	3769 [35]
$PW_{12}O_{40}^{3-}$	-196.8	89.8	-9.6	–	–	–	–	1.60	–	–	–	-99^m [5]

^{a}GIAO-B3LYP/LANL2DZ at PM3(tm) geometry.
^{b}GIAO-B3LYP/LANL2DZ at B3LYP/LANL2DZ geometry.
^{c}GIAO-B3LYP/CEP-121G at B3LYP/CEP-121G geometry.
^{d}Literature reference in brackets.
^{e}Isotropic component (ppm) of the shielding tensor; $\sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$.
^{f}Shielding anisotropy, $\Delta\sigma = \sigma_{33} - (\sigma_{22} + \sigma_{11})/2$, unscaled.
$^g\delta = \sigma_{ref} - \sigma$, relative to WO_4^{2-}.
$^h r(W) = 292$ pm, $r(O) = 170$ pm (twice the covalent radius).
$^i r_{WO} = 186.7$ pm.
$^j r_{WO} = 181.5$ pm. $\sigma = -209.1$ and -146.7 with the CSGT-LANL2DZ and GIAO-SDD method, respectively.
$^k r_{WO} = 182.1$ pm.
$^l\sigma = -370.8$ and -316.9 with the CSGT-LANL2DZ and GIAO-SDD method, respectively.
^{m}For $H_3PW_{12}O_{40}$. Calculated data differ somewhat among the various sites, due to the low symmetry of the calculated structure, and are presented as averages.

We firstly observe that all calculated shieldings are very low both as absolute values and relative to the commonly accepted standard WO_4^{2-} [1]. Even so, WS_4^{2-} is consistently predicted to be less shielded than WO_4^{2-}, as experimentally found. Using different basis sets does not improve absolute or relative shieldings (the calculated chemical shift of WS_4^{2-}, relative to WO_4^{2-}, is 181, 189 or 170 ppm with LANL2DZ, CEP-121G, and SDD, respectively). This is partly expected, since the ECP treatment cannot lead to major changes, but also implies that basis sets of different quality for the valence region do not have a large effect. Hereafter, we will present results obtained with LANL2DZ and CEP-121G.

The analysis was extended to tungsten compounds spanning the whole known shielding range. Calculated structures showed no peculiar features, and can be obtained from the authors. The data are presented in Table 1 and Fig. 1. Shielding anisotropies ($\Delta\sigma$) are also reported, since they are expected to control ^{183}W relaxation, especially at high magnetic fields [1,2].

At the DFT geometry, with both ECPs, good linear relationships spanning ca. 8000 ppm are found between calculated and experimental ^{183}W shifts. As expected [25], the slope of the correlation lines is very low, but the good quality of the fit shows that the error inherent in using ECPs is remarkably con-
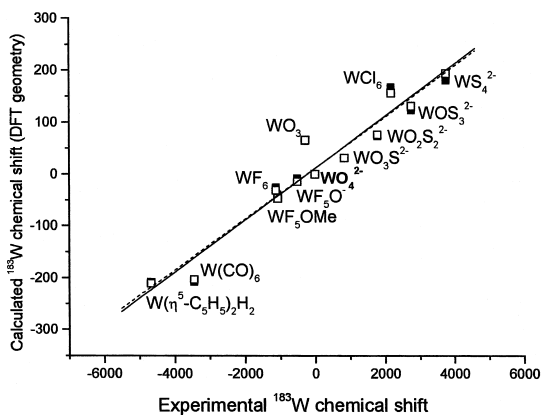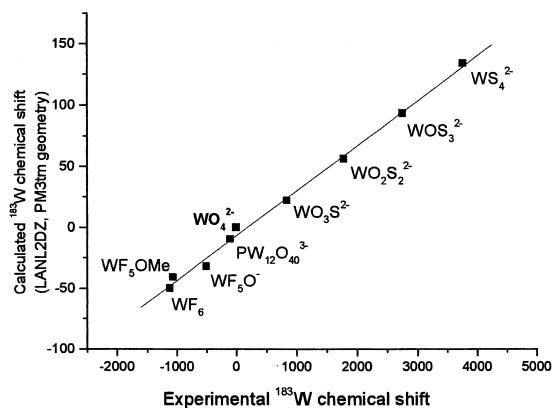

Fig. 2. ^{183}W Experimental and calculated chemical shifts at the B3LYP/LANL2DZ level with PM3(tm) geometry for W^{VI} species, including $PW_{12}O_{40}^{3-}$. Fit line: slope 0.0367 ± 0.001, intercept -7 ± 2, $r^2 = 0.998$.

stant, and hence systematic, for a wide array of species. We note that calculated shielding anisotropies should also be scaled by the appropriate slope factor (see Figs. 1 and 2) in order to estimate relaxation rates.

WO_3, $W(CO)_6$ and WCl_6 deviate most from the correlation. While the experimental value for WO_3 refers to the solid and may not be comparable with the calculated one, the discrepancy for the other two deserves further comment. Relativistic effects on the structure of $W(CO)_6$ were analyzed in detail [21,24], and the W–C distance was found to be substantially affected. It is then possible that in this particular case the level of calculation we employed does not yield a correct geometry for this species, as reflected in the calculated tungsten shielding. Moreover, there is some uncertainty as to the experimental value, since a significant difference in the W–C distance (and hence possibly in the chemical shift) exists between the experimental gas-phase and solid-state structures [21] and therefore the comparison with a value determined in solution may not be warranted. Such effects can also be expected for WCl_6, with even more heavy atoms. However, the correlation is excellent for the other W^{VI} species (still spanning 5000 ppm).

Since one of the potential applications of this study is the assignment of ^{183}W resonances in polyoxotungstates, for which a DFT optimization would be extremely demanding, we evaluated the performance of DFT vs. semi-empirical geometries by

Fig. 1. Correlation between ^{183}W experimental and calculated chemical shifts at the B3LYP/LANL2DZ (filled squares, dashed line) and B3LYP/CEP-121G levels (open squares, solid line); geometry optimized at the same respective level. Fit lines: slope 0.049 ± 0.004, intercept 11 ± 10, $r^2 = 0.965$ (LANL2DZ); slope 0.050 ± 0.004, intercept 11 ± 9, $r^2 = 0.972$ (CEP-121G).

calculating σ also at the B3LYP/LANL2DZ level, but using the PM3(tm) geometry. The overall correlation is somewhat worse, but a very good linear relationship, limited to W^{VI} species, is again found (Fig. 2), which shows that for such species the same predictive power can be achieved at a fraction of the computational expense.

The W–O distance in WO_4^{2-} differs by < 5 pm among the geometries optimized at the various levels employed. However, these small geometry changes are sufficient to entail a 20 ppm shielding difference which, when scaled by the slope factors of 0.04–0.05, amounts to no less than 400–500 ppm. Hence, it should be remarked that tungsten shieldings can only be compared at geometries optimized at the same level.

It is noteworthy that the shielding of the Keggin heteropolyoxotungstate $PW_{12}O_{40}^{3-}$ (12 equivalent tungsten sites), calculated at the PM3(tm) geometry, fits well in the correlation of Fig. 2, which shows that the semi-empirical geometry is adequate for modeling the shielding of both mono- and polynuclear W^{VI} species.

2.2. Relationship between chemical shift and atomic charge

As mentioned before, charge density/chemical shift arguments have been employed as an empirical tool for structure elucidation. It is therefore of interest to ascertain the scope of such a correlation. It should be remarked from the outset, however, that σ^p depends on the availability of certain orbitals, and this may only be indirectly or fortuitously related to the charge density or the electrostatic potential at a given nucleus (which rather depends on orbital populations).

Atomic charges at W have been calculated with the NBO [32] and ChelpG [33] partition schemes (Table 1). A fair correlation exists among W^{VI} species (Fig. 3), regardless of the net charge of the species, but fails badly for the W^0 complexes. In general, the correlation is better with NBO than with ChelpG charges (the latter are especially poor for $W(CO)_6$), but when limited to W^{VI} species the two partition schemes give correlations of very similar quality. In both cases negatively charged W nuclei
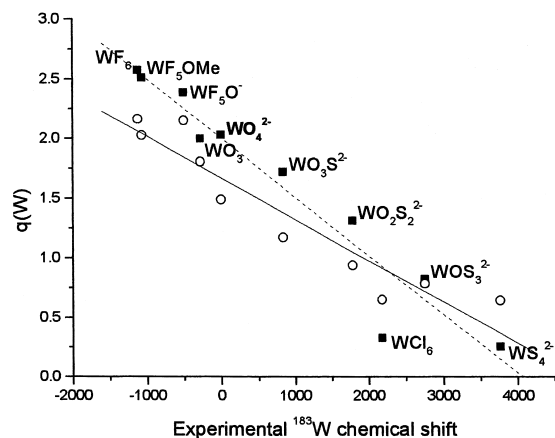

Fig. 3. ^{183}W Experimental chemical shifts and calculated atomic charges at tungsten for W^{VI} species. ChelpG charges: open circles, solid line; fit line: slope $-(3.5 \pm 0.4) \times 10^{-4}$, intercept 1.67 ± 0.07, $r^2 = 0.95$. NBO charges: filled squares, dashed line; fit line: slope $-(4.9 \pm 0.5) \times 10^{-4}$, intercept 2.00 ± 0.09, $r^2 = 0.96$.

are deshielded, in agreement with current empirical models [4].

3. Conclusion

In conclusion, we have shown that DFT/ECP methods, both at DFT and PM3(tm) geometries, correctly predict the shielding order of most tungsten species, including a symmetric Keggin-type polyoxotungstate. This finding opens the way for the prediction of ^{183}W shifts in non-symmetric polyoxotungstates [3]. Although atomic charges for species in the same formal oxidation state are fairly correlated with the shielding, a shielding calculation is preferable, albeit at an increased computational cost.

References

[1] J. Mason (Ed.), Multinuclear NMR, Plenum, New York, 1987.
[2] P.S. Pregosin (Ed.), Transition Metal Nuclear Magnetic Resonance, Elsevier, Amsterdam, 1991.
[3] C. Brevard, R. Schimpf, G. Tourné, C.M. Tourné, J. Am. Chem. Soc. 105 (1983) 7059.
[4] R. Acerete, C.F. Hammer, L.C.W. Baker, J. Am. Chem. Soc. 104 (1982) 5384, and references therein.
[5] D.B. Chesnut, in: G.A. Webb (Ed.), Annual Reports on NMR Spectroscopy, Academic Press, London, 1994.
[6] C.J. Jameson, Annu. Rev. Phys. Chem. 47 (1996) 135.

[7] D.B. Chesnut, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in Computational Chemistry, VCH, New York, 1996.
[8] A.C. De Dios, Prog. Nucl. Magn. Reson. 29 (1996) 229.
[9] H. Fukui, Prog. Nucl. Magn. Reson. 31 (1997) 317.
[10] T. Helgaker, M. Jaszunski, K. Ruud, Chem. Rev. 99 (1999) 293.
[11] V.G. Malkin, O.L. Malkina, M.E. Casida, D.R. Salahub, J. Am. Chem. Soc. 116 (1994) 5898.
[12] A.C. de Dios, E. Oldfield, J. Am. Chem. Soc. 116 (1994) 11485.
[13] A. Bagno, B. Bujnicki, S. Bertrand, C. Comuzzi, F. Dorigo, P. Janvier, G. Scorrano, Chem. Eur. J. 5 (1999) 532.
[14] A. Bagno, J. Mol. Struct. (Theochem) 418 (1997) 243.
[15] J.F. Stanton, J. Gauss, H.-U. Siehl, Chem. Phys. Lett. 262 (1996) 183.
[16] C. Adamo, V. Barone, Chem. Phys. Lett. 298 (1998) 113.
[17] M. Bühl, O.L. Malkina, V.G. Malkin, Helv. Chim. Acta 79 (1996) 742.
[18] N. Godbout, E. Oldfield, J. Am. Chem. Soc. 119 (1997) 8065.
[19] J.C.C. Chan, S.C.F. Au-Yeung, P.J. Wilson, G.A. Webb, J. Mol. Struct. (Theochem) 365 (1996) 125.
[20] M. Bühl, Chem. Phys. Lett. 267 (1997) 251.
[21] M. Kaupp, V.G. Malkin, O.L. Malkina, D.R. Salahub, Chem. Eur. J. 2 (1996) 24.
[22] M. Kaupp, O.L. Malkina, V.G. Malkin, J. Chem. Phys. 106 (1997) 9201.
[23] M. Kaupp, Chem. Eur. J. 4 (1998) 2059.
[24] G. Schreckenbach, T. Ziegler, Int. J. Quantum Chem. 61 (1997) 899.
[25] J. Ridard, B. Levy, Ph. Millie, Mol. Phys. 36 (1978) 1025.
[26] E.A. Moore, A. Healy, J. Chem. Soc., Faraday Trans. 91 (1995) 1735.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.
[28] Spartan v. 5.0, Wavefunction, 18401 Von Karman Ave., Ste. 370, Irvine, CA 92612, USA.
[29] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[30] W. Stevens, M. Krauss, H. Basch, P.G. Jasien, Can. J. Chem. 70 (1992) 612.
[31] T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, J. Chem. Phys. 105 (1996) 1052, and previous papers by the same group.
[32] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[33] C.M. Breneman, K.B. Wiberg, J. Comput. Chem. 3 (1990) 361.
[34] R. Garth Kidd, R.J. Goodfellow, in: R.K. Harris, B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, London, 1978.
[35] S.F. Gheller, T.W. Hambley, J.R. Rodgers, R.T.C. Brownlee, M.J. O'Connor, M.R. Snow, A.G. Wedd, Inorg. Chem. 23 (1984) 2519.