Notes

Structure of Chromyl Chloride (CrO_2Cl_2) in a Nitrogen Matrix and in the Solid State as determined by X-Ray Absorption Spectroscopy[‡]

Mark D. Spicer and Nigel A. Young[*,†]
Department of Chemistry, The University, Southampton SO9 5NH, UK

Chromium K-edge extended X-ray absorption fine structure (EXAFS) data for 1% chromyl chloride (CrO_2Cl_2) in a nitrogen matrix at 10 K have yielded structural data for this molecule, *d*(Cr–O) = 1.58(2) Å and *d*(Cr–Cl) = 2.10(3) Å, in good agreement with the vapour-phase electron-diffraction values, confirming the reliability of data obtained from matrix-isolation EXAFS. The EXAFS data from chromyl chloride as a cold solid at 10 and 130 K represent the first solid-state structural determination for this molecule and the refined parameters are essentially identical to those from the matrix sample but with better signal-to-noise statistics.

Extended X-ray absorption fine structure (EXAFS) has been developed into a versatile technique for the elucidation of short-range structure about the absorbing atom. Scattering atom types, co-ordination numbers, bonded and non-bonded distances may in favourable circumstances be obtained from samples in a variety of physical states and in a range of concentrations.[1,2] The lack of dependence on long-range ordering has meant that EXAFS has found its greatest usefulness in systems to which crystallographic methods are not readily applicable. Areas of study include metal sites in metalloenzymes,[3] both homogeneous and heterogeneous catalysis,[4] amorphous materials,[5] transition-metal complexes which are insufficiently stable to yield crystals of suitable quality for X-ray diffraction,[6] rare gas-doped matrices,[7] and metal atoms and clusters in rare-gas matrices.[8]

Work in these laboratories[9] has concentrated on the application of EXAFS to the study of reactive and high-temperature species isolated in cryogenic matrices, as this is often the only viable means of obtaining direct structural information in such systems. It became clear to us that it would be desirable to verify such data using a suitable compound by comparing the structural parameters derived from matrix EXAFS with those from a vapour-phase study. This approach was employed as it is commonly assumed that for co-ordinatively saturated molecular species the matrix environment is a good approximation to the gas phase, and thus represents the best means of checking the data from matrices. Chromyl chloride was chosen for this study as it is a molecular material[§] with an appreciable vapour pressure at room temperature (thus giving well defined matrix deposits), and has been characterised by a range of spectroscopic techniques[10,11] and structurally by both vapour-phase electron diffraction[12] and nozzle-beam methods.[13] Chromyl chloride has not previously been structurally characterised in the solid state and its study as a condensed solid by EXAFS would yield this information and in addition allow a comparison of EXAFS data from matrix and solid deposits. We present here a chromium K-edge EXAFS study of chromyl chloride isolated as a 1% dopant in a nitrogen matrix and as a solid at 10 and 130 K.

Results and Discussion

The X-ray absorption spectra of the dilute and neat samples were essentially identical and both had prominent pre-edge features associated with a 1s–3d transition (that becomes allowed due to mixing in non-centrosymmetric molecules) thus indicating a similar geometry for both solid and matrix-isolated species. The background-subtracted EXAFS in Fig. 1 clearly show that the signal-to-noise statistics are significantly worse (particularly at high *k*) for the matrix-isolated species as would be expected on the grounds of concentration, and it should be noted that most matrix samples are at least an order of magnitude more dilute than this. Improved signal-to-noise ratios may of course be obtained for dilute samples in matrices by recording many data sets and averaging them, but this is a tedious exercise, expensive in synchrotron time and to be avoided where possible. Curve fitting on the raw data (3–14 k) led to somewhat poorer *R* factors for the matrix data compared to the neat solid (33 *vs.* 20%), although the structural parameters obtained were essentially identical. The values obtained from the solid sample warmed to 130 K show a slight increase in the Debye–Waller factor ($2\sigma^2$) as is to be expected due to the increased thermal motion, but the interatomic distances were effectively unchanged. The slightly larger Debye–Waller factors observed for the matrix sample may reflect an increase in static disorder due to the rapid vapour deposition of the nitrogen lattice, however small differences in the values of the Debye–Waller factors may not be significant as they are the main refined amplitude parameters and as such will reflect any deficiencies in the values of other amplitude-dependent

---

[†] *Present address:* Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL.

[‡] *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

[§] In order to confirm the molecular nature of solid chromyl chloride a small portion was deposited on a CsI window at 15 K and the infrared spectrum measured and compared to those in the literature[10] for vapour-phase and argon matrix-isolated species. Bands at 995, 980, 499, 463 and 355 cm^{-1} were observed, compared to 1002.0, 991.0, 502.7, 470.0 and 355.7 cm^{-1} for the vapour and 997.8, 983.6, 501.3, 467.9 and 355.9 cm^{-1} for the argon matrix-isolated samples. The excellent agreement between these three sets of data clearly indicates that chromyl chloride is indeed a molecular material.

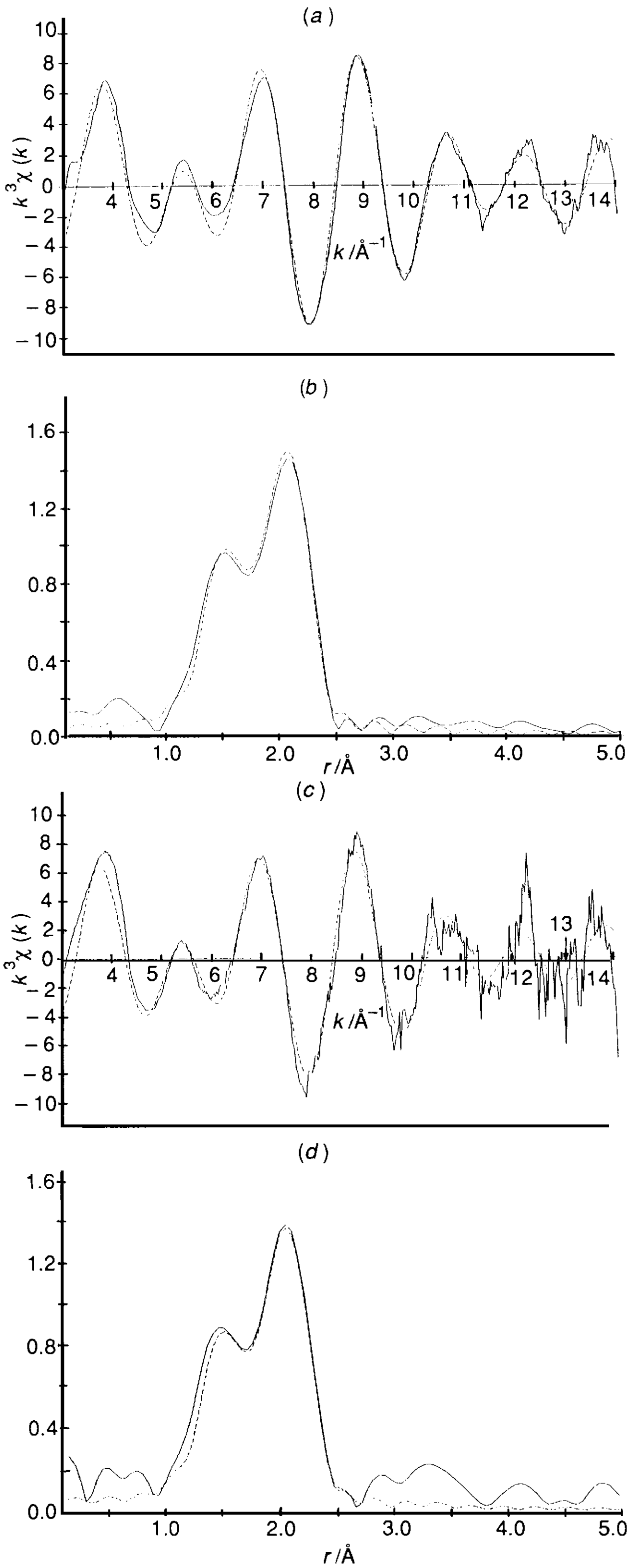

Fig. 1 EXAFS and Fourier transforms for vapour-deposited chromyl chloride at 10 K [(*a*) and (*b*)] and 1% chromyl chloride in a nitrogen matrix at 10 K [(*c*) and (*d*)]: solid line, experimental data; broken line, curved-wave theory

variables which are not included in the later stages of refinement. Fitting of Fourier-filtered data (window 0.65–2.15 Å) also yielded very similar refined parameters with better R factors and little difference between the matrix-isolated and neat solid samples. The refined parameters from all these fits are shown in Table 1 together with structural information from a previous electron-diffraction study. The error limits on the interatomic distances of ±1.5% are those estimated[14,15] to arise from systematic errors in the data collection and analysis, and are typically at least an order of magnitude greater than the statistical errors derived from the refinement process. In addition to the well defined oxygen and chlorine shells it can also be seen that in the Fourier transform for the matrix sample there is a further shell at *ca.* 3.5 Å which may arise from the matrix cavity, although attempts to model this interaction were not successful.

We have found d(Cr–O) = 1.58(2) Å and d(Cr–Cl) = 2.10(3) Å for the matrix-isolated molecule, compared to 1.581(2) and 2.126(2) Å reported by Hedberg and co-workers[2b] from an electron-diffraction experiment. (The correlations between the Cr–O and Cr–Cl shells were well within acceptable limits.) The good agreement between vapour-phase electron diffraction and matrix-isolation EXAFS is reassuring as it is widely assumed that the two phases are analogous and this therefore gives an indication of the reliability of the EXAFS data obtained from matrix-isolated samples. As a result of the limited number of determinable rotational constants the laser-induced fluorescence study[13a] of chromyl chloride in a molecular beam results only in a family of structures consistent with the electron-diffraction data. In a more recent study, Firth[13b] has pointed out that there are in fact sufficient data available to determine the non-bonded homoatomic distances d(O • • • O) and d(Cl • • • Cl) and these are in excellent agreement with those from the electron-diffraction work. These distances, however, are not determinable in our experiments and thus direct comparison is not possible. The values d(Cr–O) = 1.58(2) Å and d(Cr–Cl) = 2.10(3) Å for the condensed solid samples at both 10 and 130 K are identical within experimental/observational error to those for the matrix-isolated species indicating that in appropriate circumstances EXAFS is able to yield comparable structural parameters from a compound as a solid or in a matrix.

In conclusion this work has shown that accurate structural data may be obtained from molecular matrix-isolated species using EXAFS. In addition it indicates that, for reactive species with a tendency to aggregation, matrix EXAFS is potentially a very useful tool providing that it can be shown by either *in situ*[9b] or *ex situ* (as in this case) spectroscopic measurements (*e.g.* infrared) that the predominant matrix species are monomeric. It should be borne in mind that extrapolation from the matrix to the gas phase is not necessarily valid, especially in the light of recent work for co-ordinatively unsaturated species.[16,17] If additional spectroscopic monitoring shows that a species is molecular (*i.e.* no significant difference between solid and matrix states) then data are best collected in the solid state, saving time and effort in sample preparation, data collection and analysis with no substantial loss in integrity of the information obtained.

Experimental

Chromyl chloride (CrO_2Cl_2) (BDH) was purified by vacuum distillation and stored in darkened tap ampoules (J. Young, Acton, London) at −5 °C. The 1% mixture in nitrogen (BOC 'White Spot') was prepared using standard manometric procedures and stored in darkened bulbs. The sample deposition was controlled by poly(tetrafluoroethylene) needle valves (J. Young) and condensed onto a 0.5 mm beryllium foil (> 99.8% Goodfellows, Cambridge) held at *ca.* 10 K by a closed-cycle cryostat in the assembly described in detail elsewhere.[9]

Chromium K-edge EXAFS data were recorded in transmission mode using an order-sorting Si[111] double-crystal monochromator at 50% harmonic rejection on station 8.1 of the SERC Daresbury Laboratory Synchrotron Radiation Source operating at 2 GeV with beam currents in the range 200–230 mA. Background subtraction was carried out using PAXAS[18] by fitting the pre-edge region to a cubic polynomial and subtracting this function from the whole spectrum. The atomic component of the oscillatory part of the spectrum was approximated using spline functions and optimised by

Table 1 Refined EXAFS parameters for chromyl chloride[a]

	d(Cr–O)[b]/Å	$2\sigma^2$(Cr–O)[c]/Å^2	d(Cr–Cl)[b]/Å	$2\sigma^2$(Cr–Cl)[c]/Å^2	E_0/eV	FI[d]	R[e]
1% CrO_2Cl_2/N_2 (10 K)							
Raw data	1.581(3)	0.0108(5)	2.103(2)	0.0089(3)	12.5(4)	4.75	33.2
Fourier filtered	1.582(1)	0.0107(2)	2.106(1)	0.0086(1)	12.3(2)	0.34	10.2
Neat CrO_2Cl_2 at 10 K							
Raw data	1.578(1)	0.0074(3)	2.103(1)	0.0066(2)	11.8(3)	1.98	19.7
Fourier filtered	1.581(1)	0.0076(2)	2.106(1)	0.0069(2)	12.0(2)	0.62	12.5
Neat CrO_2Cl_2 at 130 K							
Raw data	1.579(2)	0.0090(3)	2.105(1)	0.0074(2)	11.5(3)	1.89	21.2
Fourier filtered	1.581(1)	0.0092(3)	2.105(1)	0.0076(2)	11.5(2)	0.65	13.7
Electron diffraction[f]							
Vapour phase	1.581(2)		2.126(2)				

[a] Standard deviations in parentheses. AFAC[9a] was fixed at 0.84 using chromium foil, VPI[9a] was refined and set at −2.0 V. [b] Errors arising from data collection and analysis are estimated to be ± 1.5% for interatomic distances in well defined co-ordination shells.[14,15] [c] $2\sigma^2$ is the Debye–Waller factor. [d] $\mathrm{FI} = \Sigma_i[(\chi_i^{\mathrm{T}} - \chi_i^{\mathrm{E}})k_i^3]^2$. [e] $R = [\int|\chi^{\mathrm{T}} - \chi^{\mathrm{E}}|k^3\mathrm{d}k/\int|\chi^{\mathrm{E}}|k^3\mathrm{d}k] \times 100\%$. [f] Ref. 12(*b*).

minimising chemically insignificant shells ($d < 1$ Å) in the Fourier transform. Curve fitting utilised the single-scattering curved-wave theory in the SERC Daresbury Laboratory EXCURV88 program.[19] Phase shifts and back-scattering factors were calculated by the usual *ab initio* methods[20] and found to be satisfactory without further modifications.

Acknowledgements

We thank Professor I. R. Beattie for helpful discussions and the provision of the cryostat for the EXAFS studies, Dr. W. Levason for assistance with the data collection, the director of Daresbury Laboratory for the provision of facilities and the SERC for financial support.

References

1 *X-Ray Absorption*, eds. D. C. Koningsberger and R. Prins, Wiley, New York, 1988.

2 B. K. Teo, *EXAFS: Basic Principles and Data Analysis*, Springer, Berlin, 1986.

3 R. A. Scott and M. K. Eidsness, *Comments Inorg. Chem.*, 1988, 7, 235.

4 J. Evans, in *Catalysis*, Specialist Rpt., Royal Society of Chemistry, Cambridge, 1989, vol. 8, p. 1.

5 G. N. Greaves, *Springer Ser. Chem. Phys.*, 1983, **27**, 248.

6 S. J. Higgins, W. Levason, M. C. Feiters and A. T. Steel, *J. Chem. Soc., Dalton Trans.*, 1986 317; W. Levason, J. S. Ogden and M. D. Spicer, *Inorg. Chem.*, 1989, **28**, 2128.

7 W. Malzfeldt, W. Niemann, P. Rabe and N. Schwentner, *Springer Ser. Chem. Phys.*, 1983, **27**, 203; W. Malzfeldt, W. Niemann, P. Rabe and R. Haensel, *Springer Proc. Phys.*, 1984, **2**, 445.

8 P. A. Montano, H. Purdum, G. K. Shenoy, T. I. Morrison and W. Schulze, *Surf. Sci.*, 1985, **156**, 228; W. Niemann, W. Malzfeldt, P. Rabe, R. Haensel and M. Lubcke, *Phys. Rev. B*, 1987, **35**, 1099.

9 (*a*) I. R. Beattie, N. Binsted, W. Levason, J. S. Ogden, M. D. Spicer and N. A. Young, *High Temp. Sci.*, 1989, **26**, 71; (*b*) N. A. Young and M. D. Spicer, *J. Mol. Struct.*, 1990, **222**, 77; (*c*) W. Levason, J. S. Ogden, M. D. Spicer and N. A. Young, *J. Am. Chem. Soc.*, 1990, **112**, 1019.

10 E. L. Varetti and A. Muller, *Spectrochim. Acta, Part A*, 1978, **34**, 895.

11 W. E. Hobbs, *J. Chem. Phys.*, 1958, **28**, 1220; F. A. Miller, G. L. Carlson and W. B. White, *Spectrochim. Acta*, 1959, **15**, 709; H. Stammreich, K. Kawai and Y. Tavares, *Spectrochim. Acta*, 1959, **15**, 438; M. Spoliti, J. H. Thirtle and T. M. Dunn, *J. Mol. Spectrosc.*, 1974, **52**, 146; V. E. Bondebey, *Chem. Phys.*, 1974, **18**, 293.

12 (*a*) K. J. Palmer, *J. Am. Chem. Soc.*, 1938, **60**, 2360; (*b*) C. J. Marsden, L. Hedberg and K. Hedberg, *Inorg. Chem.*, 1982, **21**, 1115.

13 (*a*) J. A. Blazy and D. H. Levy, *J. Chem. Phys.*, 1978, **69**, 2901; (*b*) S. Firth, Ph.D. Thesis, University of Southampton, 1986.

14 J. M. Corker, J. Evans, H. Leach and W. Levason, *J. Chem. Soc., Chem. Commun.*, 1989, 181.

15 K. Bornholdt, J. M. Corker, J. Evans and J. M. Rummey, *Inorg. Chem.*, 1991, **30**, 1.

16 I. R. Beattie, P. J. Jones and N. A. Young, *Chem. Phys. Lett.*, 1991, **177**, 579.

17 I. R. Beattie, P. J. Jones and N. A. Young, *Mol. Phys.*, 1991, **72**, 1309.

18 N. Binsted, PAXAS, Program for the Analysis of X-Ray Absorption Spectra, University of Southampton, 1988.

19 N. Binsted, S. J. Gurman and J. W. Campbell, EXCURV88, SERC Daresbury Laboratory Program, 1988.

20 S. J. Gurman, N. Binsted and I. Ross, *J. Phys. C*, 1984, **17**, 143; 1986, **19**, 1845.

Received 3rd *May* 1991; *Paper* 1/02107I