

# Extended X-Ray Absorption Fine Structure Spectroscopic Study of Acetone Solutions of Zinc and Lead(II) Ethylxanthate

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EXAFS and vibrational spectra of acetone solutions of zinc and lead(II) ethylxanthate have been recorded in order to correlate structural data with absorption bands in the mid-infrared region. Two ethylxanthate ions are monodentately coordinated to both zinc and lead(II) in acetone solution. Two acetone molecules are weakly coordinated to zinc to complete a tetrahedral configuration round zinc, while no acetone molecules were found in the inner sphere of the lead(II) complex. A band containing a large contribution from the C–S stretching, observed just above  $1000\text{ cm}^{-1}$  in solid zinc and lead(II) ethylxanthate, where the ethylxanthate ion is bridgingly and bidentately coordinated, respectively, shifts upwards by 20 and  $17\text{ cm}^{-1}$  in the corresponding zinc and lead(II) complexes, respectively, in acetone solution. An upward shift by about  $8\text{ cm}^{-1}$  is found in the nickel(II) and arsenic(III) complexes, where the coordination of the ethylxanthate ion remains unchanged but acetone molecules solvate the central ion to complete an octahedral configuration. No shift was found in iron(III) ethylxanthate, where the coordination remains unchanged and no acetone molecules solvate the iron(III) ion.

The interaction of alkylxanthate ions,  $\text{R-O-CS}_2^-$ , at the metal sulfide–water interface has been thoroughly studied because of its importance in the mineral processing of sulfide minerals.<sup>1</sup> Potentiometric and vibration spectroscopic studies have shown that alkylxanthate ions can be chemisorbed to zinc and lead sites in the surfaces of sphalerite and galena, respectively, in aqueous and acetone solution.<sup>2–4</sup> The vibrational spectroscopic measurements have distinguished two different ethylxanthate species on the sphalerite surfaces. One kind, type (1), is formed when the sphalerite is chemically cleaned from oxidation products by a strong complexing agent such as EDTA, and the other kind, type (2), is formed on surfaces pretreated with zinc ions.<sup>3</sup> These complexes were identified by their different vibrational spectra as determined by means of the diffuse reflectance infrared Fourier transform (DRIFT) technique.<sup>3</sup> The complexes of types (1) and (2) have strong bands in the mid-infrared region, at  $1051$ ,  $1113$  and  $1200\text{ cm}^{-1}$  and  $1033$ ,  $1113$  and  $1215\text{ cm}^{-1}$ , respectively. These band positions are compared to the bands at  $1033$ ,  $1123$  and  $1200\text{ cm}^{-1}$  for solid zinc ethylxanthate. The ethylxanthate ion bridges between two zincs and acts as a bidentate ligand in solid zinc ethylxanthate.<sup>5</sup> Two different ethylxanthate species

have also been distinguished on the surfaces of galena and synthetic lead(II) sulfide.<sup>4</sup> These complexes, denoted type (I) and (II), have bands at  $1022$ ,  $1114$  and  $1198\text{ cm}^{-1}$  and  $1006$  and  $1150\text{ cm}^{-1}$ , respectively, which are compared with the bands at  $1023$ ,  $1114$  and  $1218\text{ cm}^{-1}$  for solid lead(II) ethylxanthate. The crystal structure of lead(II) ethylxanthate is rather unusual, with one sulfur atom in the  $-\text{CS}_2^-$  entity being somewhat more strongly coordinated; the difference in Pb–S bond distance is  $0.1\text{--}0.2\text{ \AA}$ .<sup>6</sup> The cause of the band shifts, expressed in structural terms, is uncertain because no definite assignment of the coordination of the ethylxanthate ion to sulfide surfaces could be made from the presented data. Interpretations are further complicated because all bands in the mid-infrared region are highly coupled and cannot be assigned to any single bond in the ethylxanthate ion.<sup>7</sup> However, of the bands listed above, the low-frequency one has a large contribution from vibrations within the  $-\text{CS}_2^-$  entity.<sup>7</sup> This band, hereafter denoted  $\nu_a$ , is found at  $1008\text{ cm}^{-1}$  in solid potassium ethylxanthate where the  $-\text{CS}_2^-$  entity only weakly interacts with the potassium ion.

The objective of the present study is to correlate structural data with vibrational spectroscopic properties of metal ethylxanthate complexes. To achieve this, acetone solutions of zinc and lead(II) ethylxanthate have been

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studied by means of EXAFS spectroscopy and by means of vibration spectroscopy on zinc, lead(II), iron(III), nickel and arsenic(III) ethylxanthate in acetone solution and the solid state. The obtained correlations together with the vibration spectroscopic information are used to describe structural aspects of surface complexes of ethylxanthate ions.

## Experimental

### Chemicals

*Potassium ethylxanthate* was prepared from potassium hydroxide, ethanol and carbon disulfide according to a procedure described elsewhere.<sup>3</sup> The melting point was found to be 224.5–225.0°C.

*Zinc, lead(II), arsenic(III), nickel(II) and iron(III) ethylxanthates* were prepared by precipitation from an aqueous solution of potassium ethylxanthate, to which was added an aqueous solution of zinc perchlorate (G. F. Smith, analytic grade), lead(II) perchlorate (G. F. Smith, analytic grade), arsenic(III) oxide (Merck, analytic grade), nickel(II) perchlorate (G. F. Smith, analytic grade) and iron(III) chloride (Merck, analytic grade), respectively. The precipitates were washed with water. The DRIFT spectra did not indicate any impurities.

*Acetone* (Merck, analytic grade) was used as solvent without further purification.

*Collection of EXAFS data.* X-Ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), using the unfocused eight-pole wiggler beam line 4-1 under dedicated conditions, 3.0 GeV and 40–100 mA. Monochromatic radiation was obtained using a Si(111) double-crystal monochromator. The monochromator was detuned to 50% of maximum intensity to reduce high order harmonics. Three ion chambers with flowing nitrogen were used for determination of radiation intensity in the transmission mode. All spectra are an average of 2–4 scans per sample. All spectra were calibrated by the use of the internal calibration method, assigning the first inflection point of the zinc *K* and lead *L*<sub>III</sub> edges of the corresponding metal foils to 9659 and 13039 eV, respectively. The sample cells for solutions consists of two thin, ca. 40 μm, borosilicate windows pasted on titanium frames and a Vitone<sup>®</sup> spacer, 1–5 mm thick depending on absorption of the sample. The absorption of the cell windows is less than 0.15 at the used energies.

*Data processing of EXAFS data.* The EXAFS data were processed using standard procedures for pre-edge subtraction, spline fit and removal, and Fourier filtering.<sup>8</sup> Data were modelled with *ab initio* phase shift and amplitude functions. *Ab initio* data were calculated in the single scattering approximation by use of the computer program FEFF.<sup>9–11</sup> The differences in inner potential,  $\Delta E_0$ , were determined by using the Zn–O, Zn–S

and Pb–S functions to fit the EXAFS data of  $\text{Zn}(\text{H}_2\text{O})_6(\text{ClO}_4)_2(\text{s})$ ,<sup>12–14</sup>  $\text{ZnS}(\text{s})$ <sup>15</sup> and  $\text{PbS}(\text{s})$ .<sup>16</sup> Final data fitting was made by a non-linear least-squares procedure based on the curved-wave EXAFS approximation, fixing the  $\Delta E_0$  to the determined values mentioned above.<sup>8</sup>

*IR spectroscopy.* Infrared spectra were obtained using a Perkin Elmer 1760X FTIR spectrometer. The sample compartment was purged with air which had been dried and cleaned in a CO<sub>2</sub> removal dryer (Carrier and Complete Protection Ltd.). Spectra of solutions were recorded in a potassium bromide cell. All spectra were recorded at a resolution of 4 cm<sup>-1</sup> by averaging 32 scans.

## Results and discussion

*EXAFS of zinc and lead(II) ethylxanthate in acetone solution.* The Fourier transform of the EXAFS spectrum of the acetone solution of zinc ethylxanthate reveals two

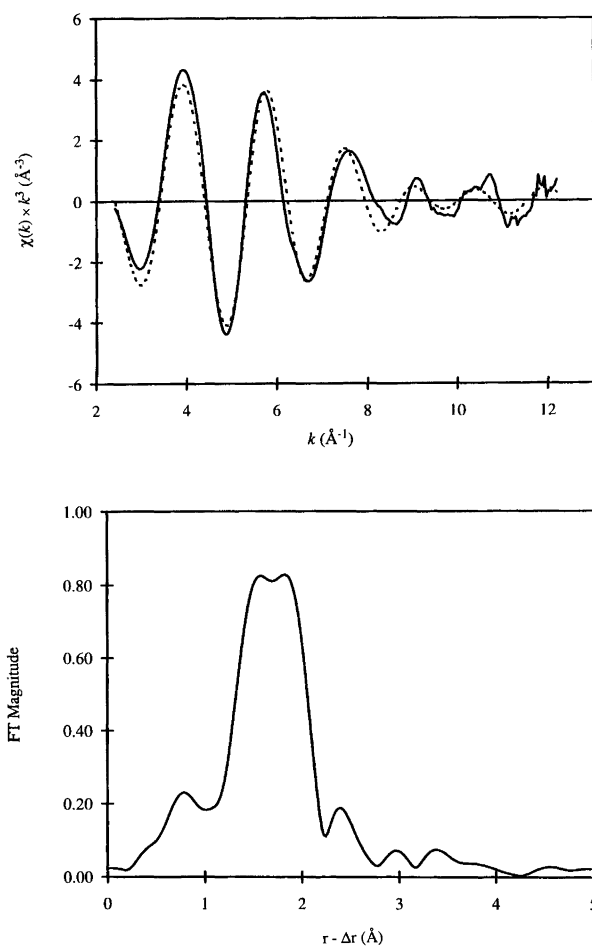


Fig. 1. The experimental EXAFS spectrum and the corresponding non-phase corrected Fourier transform (solid lines) of zinc ethylxanthate in an acetone solution and the fitted function (dashed line).

bond distances (Fig. 1). Curve-fitting and least-squares refinements using theoretical phase and amplitude parameters from FEFF gave Zn–O and Zn–S bond distances at 1.99 and 2.32 Å, respectively (Table 1 and Fig. 1). The obtained Zn–S bond distance is somewhat shorter than found in tetrahedral zinc complexes with other sulfur ligands, e.g. 2.385 Å in solid zinc ethylxanthate,<sup>5</sup> 2.34 Å in solid zinc sulfide<sup>15</sup> and 2.35 Å in tetrakis(*N,N*-dimethylthioformamide)zinc(II) trifluoromethanesulfonate,<sup>17</sup> while the Zn–O bond distance is somewhat longer than in tetrahedral zinc complexes with only oxygen donor ligands, mean 1.96 Å.<sup>18–21</sup> The short bond distance (Table 1) and low coordination numbers of both sulfur and oxygen show that the predominating species in the studied solution is a four-coordinated complex. A conductometric study showed that the conductivity of an acetone solution of zinc ethylxanthate is very low, about 0.2% of a corresponding potassium ethylxanthate solution. This shows that zinc ethylxanthate does not dissociate in acetone and that the predominating species is uncharged with both ethylxanthate ions and acetone molecules being coordinated to zinc. Hence, two ethylxanthate ions, both monodentately or one monodentately and the other bidentately, and two or one acetone molecule(s), respectively, are bound to zinc. In the absence of steric restrictions four-coordinated zinc complexes are tetrahedral.<sup>23</sup> So far, bidentate coordination of alkylxanthates is only found in square-planar and octahedral configuration,<sup>24</sup> probably because the steric strain in the four-membered M–S–C–S ring is much smaller in these configurations than in tetrahedra. Therefore, it seems likely that the complex  $\text{Zn}(\text{S}_2\text{COC}_2\text{H}_5)_2(\text{OC}(\text{CH}_3)_2)_2$  dominates in acetone solution, and that the ethylxanthate ions are monodentately coordinated to the zinc ion in this complex. It is also reasonable to assume that this complex is close to a regular tetrahedron, even though the ethylxanthate ions are more strongly coordinated to zinc than the acetone molecules. Previous studies of zinc complexes have shown that the configuration around zinc remains a regular tetrahedron even though the bond strengths of the ligands are different.<sup>23</sup> Thus, the ethylxanthate ions change coordination from bridging in solid zinc ethylxanthate to monodentate in the solvated zinc ethylxanthate complex in acetone solution, and a significant change in vibration spectrum is therefore expected.

The Fourier transform of the EXAFS spectrum of lead(II) ethylxanthate in acetone solution shows a single peak (Fig. 2). Curve-fitting and least-squares refinements

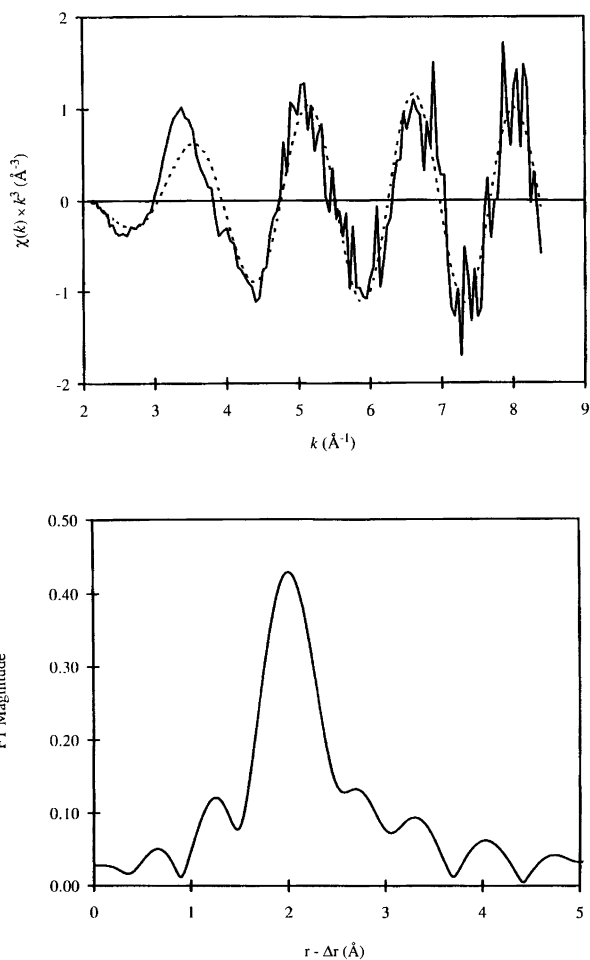


Fig. 2. The experimental EXAFS spectrum and the corresponding non-phase corrected Fourier transform (solid lines) of lead(II) ethylxanthate in an acetone solution and the fitted function (dashed line).

using theoretical phase and amplitude parameters from FEFF gave two Pb–S bonds at 2.73(2) Å (Table 1 and Fig. 2). This Pb–S distance is about the same as the shortest Pb–S distance in solid lead(II) ethylxanthate, where the Pb–S bond distances are 2.74, 2.79, 2.84 and 2.95 Å.<sup>6</sup> EXAFS of solid lead(III) ethylxanthate gave a Pb–S bond distance of 2.79 Å, thus significantly longer than found in solution. The configuration around lead in solid lead(II) ethylxanthate is pyramidal, owing to a pronounced lone electron pair effect.<sup>23</sup> Any further sulfur atoms and/or acetone molecules weakly coordinated to

Table 1. Distances in acetone solutions of zinc and lead(II) ethylxanthate as determined by EXAFS.<sup>a</sup>

| Compound  | $r(\text{M}-\text{O})/\text{Å}$ | $\sigma^2(\text{M}-\text{O})/\text{Å}^2$ | $E_0/\text{eV}$ | $n(\text{M}-\text{O})$ | $r(\text{M}-\text{S})/\text{Å}$ | $\sigma^2(\text{M}-\text{S})/\text{Å}^2$ | $E_0/\text{eV}$ | $n(\text{M}-\text{S})$ | $F_{\text{fit}}^b$ |
|---|---------------------------------|--|-----------------|------------------------|---------------------------------|--|-----------------|------------------------|--------------------|
| $\text{Zn}(\text{S}_2\text{COC}_2\text{H}_5)_2$ | 1.99                            | 0.0052                                   | -2.1            | 2 <sup>c</sup>         | 2.32                            | 0.0119                                   | -3.4            | 2 <sup>c</sup>         | 0.461              |
| $\text{Pb}(\text{S}_2\text{COC}_2\text{H}_5)_2$ |                                 |  |                 |                        | 2.73                            | 0.0063                                   | -14.4           | 2 <sup>c</sup>         | 0.242              |

<sup>a</sup>The estimated error (precision) in the distances determined by is about 0.02 for M–O and M–S distances. In addition, a systematic error (accuracy) of about 0.01 Å can be ascribed to the procedures used for the treatment of the EXAFS data.

<sup>b</sup>Weighted  $F_{\text{fit}}$ -value, for definition see Ref. 22. <sup>c</sup>Value fixed in the final refinement.

lead are not found in acetone solution. This is probably because the longest Pb–S distance is longer in acetone solution than in the solid, and that less well defined distances with large Debye–Waller factors are very hard to observe with the EXAFS technique. A conductometric study showed that the conductivity of an acetone solution of lead(II) ethylxanthate is very low, about 0.1% of that of a corresponding potassium ethylxanthate solution. This shows that lead(II) ethylxanthate does not dissociate in acetone. The ethylxanthate ions in lead(II) ethylxanthate seem therefore to be mainly monodentately coordinated to lead(II) in acetone solution, while they are mainly bidentately coordinated in the solid state, and a change in the vibration spectrum is expected.

*Vibration spectroscopic studies.* The EXAFS results show that the coordination of the ethylxanthate ion in zinc and lead(II) ethylxanthate changes from bidentate in the solids to mainly monodentate in acetone solution. A coordination change of the ethylxanthate ion is also observed in the vibration spectra. The  $\nu_a$  band at  $1033\text{ cm}^{-1}$  of solid zinc ethylxanthate is shifted upwards by  $20\text{ cm}^{-1}$

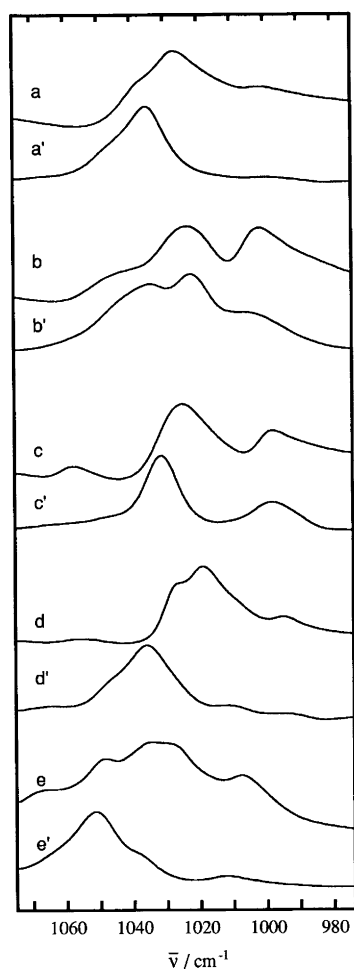


Fig. 3. FTIR spectra of solid (a) arsenic, (b) iron(III), (c) nickel(II), (d) lead(II) and (e) zinc ethylxanthate and (') in acetone solution.

when zinc ethylxanthate is dissolved in acetone, and a similar upward shift,  $17\text{ cm}^{-1}$ , is observed at the dissolution of lead(II) ethylxanthate in acetone (Fig. 3). The single and double bonds in the  $-\text{CS}_2$  entity are expected to be more well defined when an alkylxanthate ion is monodentately coordinated, as in acetone solution, compared with bidentately and bridgingly coordinated alkylxanthate ions, where electrons are delocalised over the  $-\text{CS}_2$  entity.

The vibration spectra of nickel(II), iron(III) and arsenic(III) ethylxanthate in both the solid state and acetone solution have been recorded because the ethylxanthate ion is expected to maintain its basic configuration in the respective complexes at dissolution in acetone. The ethylxanthate ion is bidentately coordinated to nickel(II)<sup>25</sup> and iron(III),<sup>26</sup> while it is monodentately coordinated to arsenic(III).<sup>27</sup> The central ion is expected to be solvated by acetone in the nickel(II) and arsenic(III) ethylxanthate complexes, while iron(III) coordinates six sulfur atoms in the complex, and acetone is not expected to enter the inner sphere in this complex.

The  $\nu_a$  band of solid iron(III) ethylxanthate remains unshifted in acetone solution, as expected (Fig. 3), while upward shifts of  $8\text{ cm}^{-1}$  are observed at the dissolution of nickel(II) and arsenic(III) ethylxanthate in acetone owing to the solvation of the central ions and a weakening of the M–S bonds. The coordination number of the nickel(II) and arsenic(III) increases to six at solvation. This is seen by a colour change from brownish red to deep green on dissolving nickel(II) ethylxanthate, where most probably two acetone molecules are coordinated to nickel in the axial positions. A similar change from three- to six-coordination is expected to take place for arsenic(III) ethylxanthate in acetone.

*Coordination of ethylxanthate ions to mineral surfaces.* This study has shown that a change in the coordination of the ethylxanthate ion is reflected by a shift of the  $\nu_a$  absorption band. It is therefore possible to postulate the kind of coordination of the alkylxanthate ion in solution of a metal ethylxanthate complex or on a surface from the shift in the  $\nu_a$  absorption band.

The surface complex of type (1) on sphalerite shows a fairly large upward shift,  $18\text{ cm}^{-1}$ , as compared to solid zinc ethylxanthate, indicating that the ethylxanthate ion in this complex is most probably monodentately coordinated to the surface, as proposed previously.<sup>3</sup> The infrared spectrum of the type (2) complex resembles that of solid zinc ethylxanthate with no shift of the  $\nu_a$  band. This suggests that the structure and the electron distribution in the  $-\text{CS}_2$  entity of the surface complex is similar to that of solid zinc ethylxanthate and that the type (2) complex is bidentately or bridgingly coordinated to zinc ions in the sphalerite surface.

The surface complex of type (I) on galena shows a downward shift of only  $1\text{ cm}^{-1}$  of the  $\nu_a$  band, indicating that the ethylxanthate ion in this complex is most probably approximately bidentately coordinated to the lead(II)

ions, just as in solid lead(II) ethylxanthate.<sup>6</sup> The infrared spectrum of the type (II) shows a negative shift of  $17\text{ cm}^{-1}$  of the  $\nu_a$  band as compared to solid lead(II) ethylxanthate. The origin of this downward shift cannot be explained by the present measurements. However, it may be noted that the surface complex of type (II) is formed in acetone, and that it is easily washed off the surface with water, which might be an indication of a primarily electrostatic interaction with the surface. This hypothesis is also supported by the fact that the  $\nu_a$  frequency,  $1006\text{ cm}^{-1}$ , is close to that of solid potassium ethylxanthate,  $1008\text{ cm}^{-1}$ , and of an aqueous solution of potassium ethylxanthate,  $1009\text{ cm}^{-1}$ , where the ethylxanthate ion is only influenced by pure electrostatic forces.

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## References

1. Somasundaran, P. and Moudgil, B. M. *Reagents in Mineral Technology*, Marcel Dekker Inc., New York 1988.
2. Sun, Z. *Surface Reactions in Aqueous Metal Sulfide Systems*, Thesis, Luleå University of Technology, Luleå 1991.
3. Persson, P., Malmensten, B. and Persson, I. *J. Chem. Soc., Faraday Trans. 87* (1991) 2769.
4. Persson, P. and Persson, I. *J. Chem. Soc., Faraday Trans. 87* (1991) 2779 and references therein.
5. Ikeda, T. and Hagihara, H. *Acta Crystallogr. 21* (1966) 919.
6. Hagihara, H. and Yamashita, S. *Acta Crystallogr. 21* (1966) 350.
7. Valli, M., Mink, J. and Sandström, M. *To be published*.
8. George, G. N. and Pickering, I. J. *EXAFSPAK – A Suite of Computer Programs for Analysis of X-Ray Absorption Spectra*, Stanford, CA 1993.
9. Rehr, J. J., Albers, R. C. and Zabinsky, S. I. *Phys. Rev. Lett. 69* (1992) 3397.
10. Rehr, J. J., Mustre de Leon, J., Zabinsky, S. I. and Albers, R. C. *J. Am. Chem. Soc. 113* (1991) 5135.
11. Mustre de Leon, J., Rehr, J. J., Zabinsky, S. I. and Albers, R. C. *Phys. Rev. B 44* (1991) 4146.
12. Ohtaki, H., Yamaguchi, T. and Maeda, M. *Bull. Chem. Soc. Jpn. 49* (1976) 701.
13. Goggin, P. L., Johansson, G., Maeda, M. and Wakita, H. *Acta Chem. Scand., Ser. A 38* (1984) 625.
14. Wakita, H., Johansson, G., Sandström, M., Goggin, P. L. and Ohtaki, H. *J. Solution Chem. 20* (1991) 643.
15. Yamanaka, T. and Tokomani, M. *Acta Crystallogr., Sect. B 41* (1985) 298.
16. Noda, Y., Masumoto, K., Oba, S., Saito, Y., Toriumi, K., Iwata, K. and Shibuya, I. *Acta Crystallogr., Sect. C 43* (1987) 1443.
17. Persson, I., Sandström, M., Stålhandske, C. M. V. and Stålhandske, C. *To be published*.
18. Eggers-Borkenstein, P., Priggemeyer, S., Krebs, B., Henkel, G., Simonis, U., Pettifer, R. F., Nolting, H.-F. and Hermes, Ch. *Eur. J. Biochem. 186* (1989) 667.
19. Giovanoli, R., Oswald, H. R. and Feitknecht, W. *Helv. Chim. Acta 49* (1966) 1971.
20. Schnering, H. G. *Z. Anorg. Allg. Chem. 330* (1964) 170.
21. Nørlund Christensen, A. *Acta Chem. Scand. 23* (1969) 2016.
22. Pickering, I. J., George, G. N., Dameron, C. T., Kurz, B., Winge, D. R. and Dance, I. G. *J. Am. Chem. Soc. 115* (1993) 9498.
23. Wells, A. F. *Structural Inorganic Chemistry*, Oxford University Press, Oxford 1990, chap. 51.
24. Winter, G. *Rev. Inorg. Chem. 2* (1980) 253.
25. Franzini, M. *Z. Kristallogr. 118* (1963) 393.
26. Hoskins, B. F. and Kelly, B. P. *Chem. Commun.* (1970) 45.
27. Carri, G. and Gottardi, G. *Z. Kristallogr. 113* (1960) 373.

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