

Unusual route for preparation of manganese(II), cobalt(II), zinc(II) and cadmium(II) carbonate compounds: synthesis and spectroscopic characterizations

MOAMEN S REFAT^{†,*} and MOHSEN M AL-QAHTANI[†]

Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Kingdom Saudi Arabia

[†]Department of Chemistry, Faculty of Science, Suez Canal University, Port Said 42111, Egypt

MS received 4 February 2010; revised 7 April 2010

Abstract. The manganese(II) carbonate, $\text{MnCO}_3 \cdot \text{H}_2\text{O}$, cobalt(II) carbonate, $\text{CoCO}_3 \cdot 4\text{H}_2\text{O}$, zinc(II) carbonate, ZnCO_3 and cadmium(II) carbonate, CdCO_3 , respectively, were synthesized by a new simple unusual route during the reaction of aqueous solutions of MnX_2 , CoX_2 , ZnX_2 and CdX_2 , where ($\text{X} = \text{Br}^-$ and ClO_4^-) with urea at high temperature within $\sim 90^\circ\text{C}$ for 6 h. The infrared spectra of the reaction products clearly indicate the absence of the bands of urea, but show the characteristic bands of ionic carbonate, CO_3^{2-} . A general mechanism describing the preparation of manganese(II), cobalt(II), zinc(II) and cadmium(II) carbonate compounds are discussed.

Keywords. $\text{MnCO}_3 \cdot \text{H}_2\text{O}$; $\text{CoCO}_3 \cdot 4\text{H}_2\text{O}$; ZnCO_3 ; CdCO_3 ; infrared spectra.

1. Introduction

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea has a melting point of 132°C , soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde–urea resin (plastics) (Feldman and Barbalata 1996), barbiturates (Finar 1973), and fertilizers (Rahman *et al* 1994; Wang and Douglas 1996; George *et al* 1997; Yerokun 1997). Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine (Miyagawa 1986; Heinig 1996; Gnewuch and Sosnovsky 1997). For example, metal–urea complexes have a pharmaceutical application that the platinum–urea complex was recorded a significant effect as an antitumor agent (Sugimura *et al* 1990).

Yamaguchi and Stewart (Stewart 1957; Yamaguchi *et al* 1957) were assigned all of the observed frequencies in the spectra of urea and urea- d_4 . The two vibrations of the frequencies at 1686 and 1603 cm^{-1} were assigned as the 1686 cm^{-1} band due to CO stretching vibration and the 1603 cm^{-1} band for NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-1} , the contribution of the NH_2 bending motion is greater than that of CO stretching motion. The infrared bands of urea- d_4 observed at 1245 and 1154 cm^{-1} are

assigned to ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The 1464 cm^{-1} frequency of urea is assigned to the CN stretching vibration. The corresponding frequency of urea- d_4 is observed at 1490 cm^{-1} . The 1150 cm^{-1} band is assigned to NH_2 rocking vibrations.

The reactions between transition metal ions and urea at room temperature have been studied extensively (Schafer and Curran 1966; Barbier and Hugel 1974; Zarli *et al* 1976; Barbier and Hugel 1977; Srivastava and Aravindakshah 1983). The infrared spectra of these complexes clearly indicated that urea molecule behaves as a monodentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom.

The nature of the reaction products depend strongly on the type of metal ions and hence the metal salt used. The novelty in our previous studies (Nour *et al* 1997; Sadeek *et al* 2004; Refat *et al* 2004a, b; Refat 2004; Teleb *et al* 2004; Sadeek and Refat 2005; Refat and Sadeek 2005; Refat 2005; Teleb and Refat 2006) were oriented to the reaction of urea ligand with different metals such as Co(II), Pb(II), Sn(II), Cr(III), Fe(III), Au(III), Sn(IV), V(V) and Mo(IV) at high temperatures which demonstrate that the types of metal ions beside their anions have a pronounced effect on the nature of the reaction products. The published papers were trended for the reaction of urea with different metal salts at elevated temperature lead to discovering a novel method for preparation PbCO_3 and CoCO_3 (Refat *et al* 2004a), lanthanide carbonates (Refat 2004; Teleb and Refat 2006), limonite,

*Author for correspondence (msrefat@yahoo.com)

FeO(OH) (Sadeek 2004), $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ (Sadeek and Refat 2005), $\text{SnOCl}_2 \cdot 2\text{H}_2\text{O}$ (Teleb *et al* 2004), (Cr_2O_3 , MnO_2 , MoO_3 and WO_3) oxides resulted from a novel oxidation reduction reaction between (K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$), KMnO_4 , Na_2MoO_4 and Na_2WO_4 , respectively, with urea in an aqueous solution at $\sim 85^\circ\text{C}$ (Teleb and Refat 2006).

The present study was undertaken to detect the nature of the reaction products obtained during the reaction of urea with MnX_2 , CoX_2 , ZnX_2 and CdX_2 ($\text{X} = \text{Br}^-$ and ClO_4^-) with urea at $\sim 90^\circ\text{C}$ for 6 h in aqueous media. The reaction products were isolated as solids and characterized by elemental analysis, infrared spectroscopy.

2. Experimental

All chemicals used throughout this work were Analar or extra pure grade. $\text{MCO}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn(II)}$, Co(II) , Zn(II) or Cd(II) ; $n = 1$ for MnCO_3 or $n = 4$ for CoCO_3) were prepared by mixing an aqueous solutions (75 ml) of 0.1 M of urea with 0.01 M of the respective Mn(II), Co(II), Zn(II) or Cd(II) salts. The acidic radical for all starting salts is $\text{MnX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$ and ClO_4^- , $n = 4$ or 6), $\text{CoX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$ and ClO_4^- , $n = x\text{H}_2\text{O}$ or 6), $\text{ZnX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$ and ClO_4^- , $n = 2$ or 6) and cadmium(II) salts, $\text{CdX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$ and ClO_4^- , $n = 4$ or $x\text{H}_2\text{O}$). The mixtures were heated at $\sim 90^\circ\text{C}$ for 6 h in a water bath. The solid compounds were filtered off, washed several times with hot water, dried at 80°C in an oven for 3 h and then placed in *vacuo* over silica gel. The yields of the obtained Mn(II), Co(II), Zn(II) and Cd(II) carbonates were varied in the range 70–80% depending upon the type of metal as well as on the counter ions associated with the metal ion. The average of elemental analysis for $\text{MCO}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn(II)}$, Co(II) , Zn(II) and Cd(II)) obtained during the reaction of urea with the respective metal salts almost the same and indicate the absence of nitrogen element. Analysis of the solid products obtained as follows

$\text{MnCO}_3 \cdot \text{H}_2\text{O}$ ($M_{\text{wt.}} = 132.95$)

Found (C = 8.95%, H = 1.44%, Mn = 41.22%, $\text{CO}_3^{2-} = 45.05\%$).

Calcd (C = 9.02%, H = 1.50%, Mn = 41.32%, $\text{CO}_3^{2-} = 45.13\%$). $\text{CoCO}_3 \cdot 4\text{H}_2\text{O}$ ($M_{\text{wt.}} = 190.94$).

Found (C = 6.17%, H = 4.10%, Co = 30.45%, $\text{CO}_3^{2-} = 31.11\%$).

Calcd (C = 6.28%, H = 4.19%, Co = 30.86%, $\text{CO}_3^{2-} = 31.42\%$). ZnCO_3 ($M_{\text{wt.}} = 125.38$).

Found (C = 9.48%, Zn = 52.08%, $\text{CO}_3^{2-} = 47.77\%$).

Calcd (C = 9.57%, Zn = 52.14%, $\text{CO}_3^{2-} = 47.85\%$). CdCO_3 ($M_{\text{wt.}} = 172.42$).

Found (C = 6.89%, Cd = 65.11%, $\text{CO}_3^{2-} = 34.62\%$).

Calcd (C = 6.96%, Cd = 65.19%, $\text{CO}_3^{2-} = 34.80\%$).

Carbonate content in the four compounds were determined by dissolving a sample of each product in excess standard HCl and the excess of HCl was determined using standard sodium carbonate (Vogel 1987). The percentage of manganese, cobalt, zinc and cadmium in the compounds were determined by gravimetric method till constant weight and stable formula. The infrared spectra of urea, all reactants and products were recorded in KBr discs using a Shimadzu FT-IR spectrophotometer.

3. Results and discussion

The reaction of aqueous solutions of urea with perchlorate and bromide salts of manganese(II), cobalt(II), zinc(II) and cadmium(II) at *ca.* $\sim 90^\circ\text{C}$ produces a brown, red, white solid crystalline products, respectively. The infrared spectra of urea as well as the reaction products of different manganese(II), cobalt(II), zinc(II) and cadmium(II) salts with urea at high temperature are obtained from KBr discs. These spectra are shown in figure 1a–e. The band assignments for the products are given in table 1. The infrared spectra show no bands due to any of the reactants and of coordinated urea, but instead, a group of bands characteristic for the ionic carbonate, $(\text{CO}_3)^{2-}$, is appeared (Nakamoto 1978). Based on this fact, along with that obtained from elemental analysis data as well as the volumetric determination of $(\text{CO}_3)^{2-}$ group with standard solution of HCl; beside that the infrared spectra of the commercially obtained $\text{MnCO}_3 \cdot n\text{H}_2\text{O}$, $\text{CoCO}_3 \cdot n\text{H}_2\text{O}$, ZnCO_3 and CdCO_3 are the same as that of the reaction products. The products obtained were identified as $\text{MnCO}_3 \cdot \text{H}_2\text{O}$, $\text{CoCO}_3 \cdot 4\text{H}_2\text{O}$, ZnCO_3 and CdCO_3 . The infrared assignments agree quite well with those known (Nakamoto 1978) for the ionic carbonate $(\text{CO}_3)^{2-}$.

Previous studies (Nour *et al* 1997; Sadeek *et al* 2004; Refat *et al* 2004a, b; Refat 2004; Teleb *et al* 2004; Sadeek and Refat 2005; Refat and Sadeek 2005; Refat 2005; Teleb and Refat 2006) indicated that the nature of the reaction product obtained from the reaction of metal ions with urea at high temperature depends on the type of metal ion, and in some cases on the nature of the metal salts used.

At room temperature the coordination compounds of manganese(II) ion with urea have been studied extensively (Antonienko and Nuger 1966; Stancheva 1970; Barbier and Hugel 1974; Yamagata *et al* 1989) and it was found that urea coordinates to Mn(II) ions at room temperature via its oxygen atom, forming the $[\text{Mn(urea)}_4]\text{X}_2$ octahedral complex (Barbier and Hugel 1974). However, The Mn(II)-urea compounds of the type $\text{Mn(urea)}_6\text{X}_2$ ($\text{X} = \text{Br}^-$, I^- , and ClO_4^-) are also known. They are of ionic nature and could be written as $[\text{Mn(urea)}_6]\text{X}_2$. These compounds are of high-spin octahedral structure with urea coordinated to manganese through its oxygen atom. At high temperature the role of Mn(II) ions in decomposing

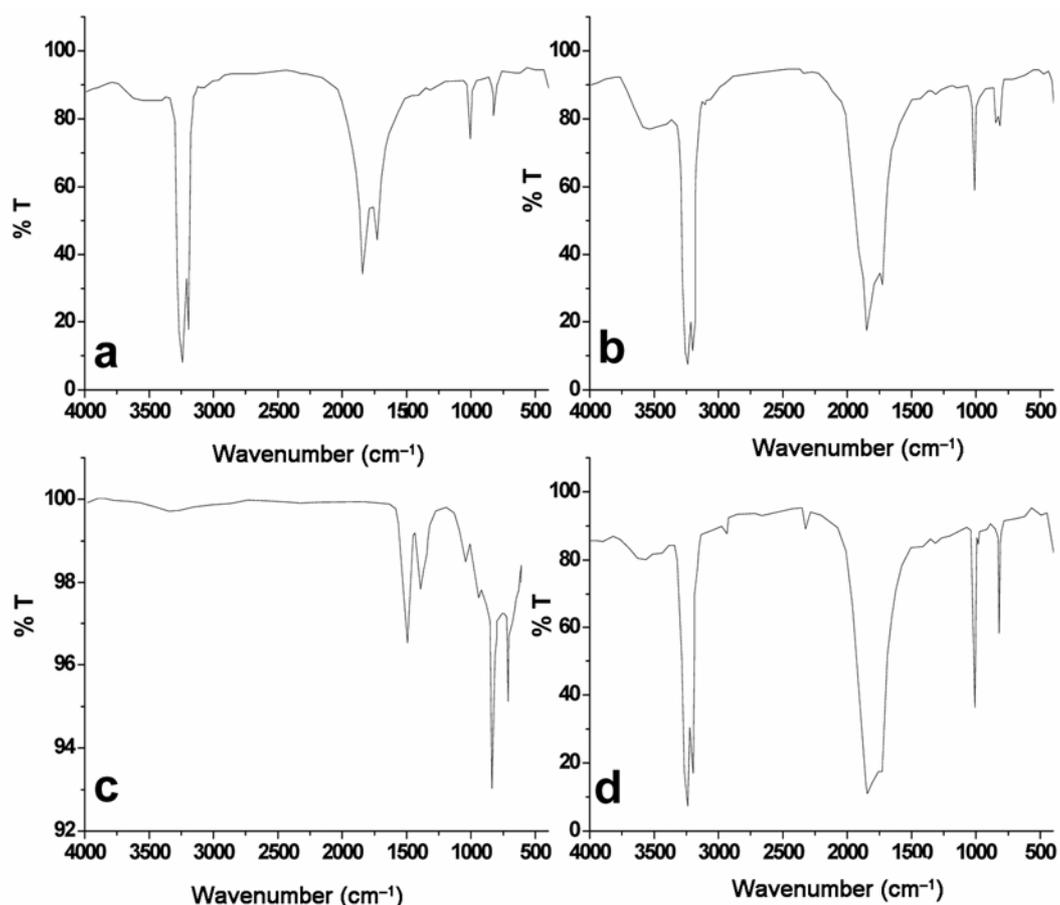
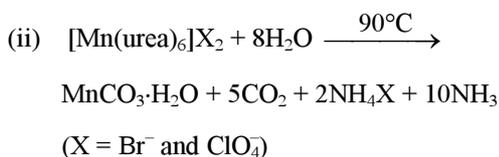
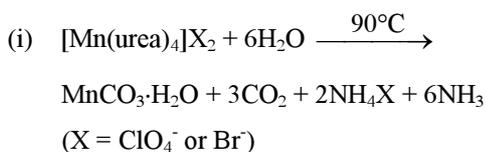
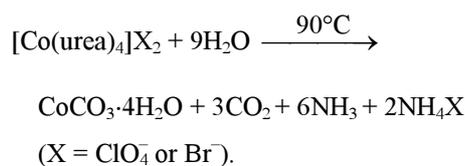


Figure 1. Infrared spectra of the products obtained from the reaction of (a) MnX_2 , (b) CoX_2 , (c) ZnX_2 and (d) CdX_2 where ($\text{X} = \text{Br}^-$ and ClO_4^-) with urea at high temperature.

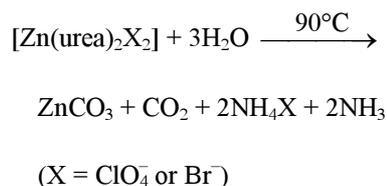
the coordinated urea in the form of $[\text{Mn}(\text{urea})_4]\text{X}_2$ or $[\text{Mn}(\text{urea})_6]\text{X}_2$ could be understood according to the following reactions



The X-ray studies on cobalt(II) salt-urea complexes (Galdecki and Golinski 1961; Kuznetsov *et al* 1967; Rau *et al* 1971) indicated that the $\text{Co}(\text{NO}_3)_2$ reacts with urea at room temperature to form the complex $[\text{Co}(\text{urea})_4](\text{NO}_3)_2$; in these complexes urea coordinates to Co(II) via its oxygen atom. The role of Co(II) ions in decomposing the coordinated urea at high temperature may be understood as follows



At room temperature the coordination compounds of zinc(II) ion with urea have been studied extensively (Penland *et al* 1957; Yar and Lessinger 1995) and it was found that, in these complexes, urea coordinated through its oxygen atom forming the $[\text{Zn}(\text{urea})_2\text{X}_2]$ where ($\text{X} = \text{Cl}^-$, NO_3^- or CH_3COO^-). At high temperature the role of Zn(II) ions in decomposing the coordination urea in the form of $[\text{Zn}(\text{urea})_2\text{X}_2]$ could be understood as follows



Adducts of $\text{ZnX}_2 \cdot 2\text{urea}$ ($\text{X} = \text{Cl}$, Br , I), $\text{CdX}_2 \cdot 2\text{urea}$ ($\text{X} = \text{Br}$, I), $\text{CdX}_2 \cdot \text{urea}$ ($\text{X} = \text{Cl}$, Br , I) and $\text{HgX}_2 \cdot \text{urea}$

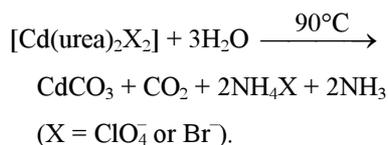
Table 1. Infrared frequencies (cm^{-1}) and assignments of the products obtained from the reaction of (a) MnX_2 , (b) CoX_2 , (c) ZnX_2 and (d) CdX_2 , where ($\text{X} = \text{Br}^-$ and ClO_4^-) with urea at high temperature.

Frequencies* (cm^{-1})				
a	b	c	d	Assignments
2964, 2925	2924	–	3070, 2954	$\nu(\text{O-H}); \text{H}_2\text{O}$
1463, 1376	1464, 1378	1503, 1391	1468	$\nu(\text{C-O}); \text{CO}_3^{2-}$
1070	1079	1060	1077	
863	866	833	860, 836	$\delta(\text{OCO}); \text{CO}_3^{2-}$
726	724, 732, 722	708	723	

*br, broad; m, medium; sh, shoulder; s, strong; w, weak; ν , stretching; δ , bending

($\text{X} = \text{Cl}, \text{Br}$) have been characterized (Maria and Santos 1988). The shifts of the stretching vibrations to low frequency (νCO) and to high frequencies (νCN and νNH) indicated that urea is oxygen-bonded to the metals.

At high temperature the role of $\text{Cd}(\text{II})$ ions in decomposing the coordination urea in the form of $[\text{Cd}(\text{urea})_2\text{X}_2]$ could be understood as follows



The $(\text{CO}_3)^{2-}$ ion is planar and therefore, belongs to the D_{3h} symmetry. It is expected to display four modes of vibrations, $\text{A}'_1 + \text{A}'_2 + 2\text{E}'$ (E' is a double degenerate motion). The vibration A'_1 is only Raman active while the other ν_2 , ν_3 and ν_4 are infrared active. The stretching vibrations of the type $\nu(\text{C-O})$, $\nu_3(\text{E}')$ is observed as a strong broad band in the range of $1503\text{--}1376 \text{ cm}^{-1}$ while the stretching vibration $\nu(\text{C-O})$, $\nu_1(\text{A}'_1)$ is observed in the region $\sim 1070 \text{ cm}^{-1}$ as a medium-to-weak band. It should be indicated here that this motion (A'_1) should be infrared inactive, its weak appearance in the spectrum of $\text{MCO}_3 \cdot n\text{H}_2\text{O}$ could be related to weak solid–solid interactions which causes the symmetry of CO_3^{2-} to be lowered than D_{3h} . The out of plane of vibration $\delta(\text{OCO})$, $\nu_2(\text{A}'_2)$ is observed in the range of $\sim 860 \text{ cm}^{-1}$ as a strong band, while the angle deformation bending vibration $\delta(\text{OCO})$, $\nu_4(\text{E}')$ appear in the range of $744\text{--}708 \text{ cm}^{-1}$ as a medium strong. The infrared spectra of metal(II) carbonate, $\text{MCO}_3 \cdot n\text{H}_2\text{O}$ show that some of these products clearly have an uncoordinated water. The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $\sim 3000 \text{ cm}^{-1}$ (table 1).

References

- Antonienko N S and Nuger J A 1966 *Z. Neorg. Chim.* **11** 1072
- Barbier J P and Hugel R 1974 *Inorg. Chim. Acta* **10** 93
- Barbier J P and Hugel R P 1977 *J. Inorg. Nucl. Chem.* **39** 2283
- Feldman D and Barbalata A 1996 *Synthetic polymers* (London: Chapman & Hall)
- Finar I L 1973 *Organic chemistry* (London: Longman Group Limited) p 460
- Galdecki Z and Golinski B 1961 *Zeszyty Nauk. Politech. Lodz. Chem.* **10** 15
- George S, Chellapandian M, Sivasankar B and Jayaraman K 1997 *Bioprocess Eng.* **16** 83
- Gnewuch C T and Sosnovsky G 1997 *Chem. Rev.* **97** 829
- Heinig R 1996 *SOFW J.* **122** 998
- Kuznetsov V G, Kondrat'eva N G and Druzhinin I G 1967 *Russ. J. Inorg. Chem.* **12** 665
- Maria R M C and Santos C A 1988 *Thermochim. Acta* **125** 295
- Miyagawa C I 1986 *Drug Intell. & Clin. Pharma.* **20** 527
- Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley Interscience) 3rd edn.
- Nour E M, Tebeb S M, Al-Khososy N A and Refat M S 1997 *Synth. React. Inorg. Met.-Org. Chem.* **27** 505
- Penland R B, Mizushima S, Curran C and Quagliano J V 1957 *J. Am. Chem. Soc.* **79** 1575
- Rahman M J, Bozadjiev P and Polovski Y 1994 *Fert. Res.* **38** 89
- Rau T F, Kurkutova E N, Kondrat'eva N G and Kinderov A P 1971 *Russ. J. Inorg. Chem.* **16** 933
- Refat M S 2004 *Synth. React. Inorg. Met.-Org. Chem.* **34** 1605
- Refat M S and Sadeek S A 2005 *Latvian J. Chem.* **4** 343
- Refat M S, Sadeek S A and Nasr D E 2005 *Bull. Chem. Technol. Maced.* **24** 153
- Refat M S, Tebeb S M and Sadeek S A 2004a *Spectrochim. Acta* **A60** 2803
- Refat M S, Sadeek S A and Tebeb S M 2004b *J. Argen. Chem. Soc.* **92** 23
- Sadeek S A and Refat M S 2005 *J. Coord. Chem.* **58** 1727
- Sadeek S A, Refat M S and Tebeb S M 2004 *J. Korea, Chem. Soc.* **48** 358
- Schafer M and Curran C 1966 *Inorg. Chem.* **5** 256
- Srivastava P C and Aravindaksaahn C 1983 *Z. Phys. Chem. Leipzig* **264** 61
- Stancheva P 1970 *Nauch. Tr. Vissk. Pedagog. Inst. Plovdiv* **8** 103
- Stewart J E 1957 *J. Chem. Phys.* **26** 248
- Sugimura M, Kameyama Y, Hashimoto T, Kobayashi T and Muramatsu S 1990 *Chem. Abs.* **112** 63
- Tebeb S M and Refat M S 2006 *Bull. Chem. Technol. Maced.* **25** 57

- Teleb S M, Refat M S, Sadeek S A 2004 *Ukrainian Chem. J.* **68** 35
- Vogel 1987 *Qualitative inorganic analysis* (New York: John Wiley & Sons, Inc)
- Wang X J and Douglas L A 1996 *Agrochimica* **40** 209
- Yamagata K, Saito Y and Abe T 1989 *J. Phys. Soc. Jpn.* **58** 752
- Yamaguchi A, Miyazawa T, Shimanouchi T and Mizushima S 1957 *Spectrochim. Acta* **10** 170
- Yar O and Lessinger L 1995 *Acta Cryst. Sect. C Cryst. Struct. Commun.* **C51** 2282
- Yerokun O A 1997 *S. Afr. J. Plant Soil* **14** 63
- Zarli B, Dall'Olio G and Sindellari L 1976 *J. Inorg. Nucl. Chem.* **38** 491