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Some Transiton Metal Complexes of Isothiazole

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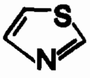
Complexes of isothiazole (IT) with certain transition metals are reported. The complexes of the divalent metal ions include $MHal_2(IT)_2$ *(M = Cu or Co; Hal = Cl or Br),* $NiBr_2(IT)_2$ *and* $NiCl_2(IT)_4$; $MX_2(IT)_4$ *(M = Cu; X =* NO_3 *or* ClO_4*) and* $Cu(NO_3)_2(IT)_2$; $M(ClO_4)_2(IT)_6$ *(M = Ni or Co) and* $Cu(ClO_4)_2(IT)_4$; *trans–*$Co(NCS)_2(IT)_4$ *and cis–*$PtCl_2(IT)_2$*. Infrared spectra, magnetic properties, conductance data, and X-ray powder patterns of the complexes have been recorded and the bonding mode of the ligand is discussed. The bonding occurs through the nitrogen atom and not the sulfur atom of the isothiazole.*

Introduction

The isomeric ligands thiazole (T) and isothiazole (IT) have both



(T)

(IT)

sulfur and nitrogen as potential donor sites for bonding to transition metal ions. In the complexes of thiazole[1,2] and its 4-alkyl and 2,4-dialkyl derivatives[2] coordination was found to occur exclusively through the nitrogen atom. In this paper the complexing properties of the relatively new heterocyclic compound isothiazole towards copper(II), nickel(II), cobalt(II), and platinum(II) are examined.

Experimental Section

Isothiazole (IT), b.p. 114°, was obtained from Raylo Chemical Ltd., Edmonton, Alta., Canada, and 2,2-dimethoxypropane from Eastman Organic Chemicals, Rochester, N.Y., U.S.A. Nitromethane was dried over calcium chloride and redistilled. All other chemicals were of reagent grade and used without further purification.

Infrared spectra were recorded as mulls in Nujol or hexachlorobutadiene between CsBr plates on a Perkin-Elmer 457 spectrophotometer, frequency being calibrated with a polystyrene film. Magnetic measurements were made by the Gouy method, using $Hg[Co(CNS)_4]$ as standard.[3] Conductance was measured with a Philips GM 4144 measuring bridge. X-ray powder patterns were recorded on a Philips Norelco X-ray powder diffractometer using FeK_α radiation with a Mn filter. Chemical analyses were performed by Baron Consulting Co., Orange, Conn., U.S.A. Analytical data and some phisical properties of the new compounds prepared are shown in Table I. Infrared and X-ray powder pattern data of the complexes are tabulated in Tables II and III. All the products were air dried, unless otherwise stated in the text.

Preparation of Compounds. $CuCl_2(IT)_2$. An alcoholic solution of isothiazole (3.41 g in 50 ml, 40 mmoles) was added to an alcoholic solution of $CuCl_2 . 2H_2O$ (1.71 g in 150 ml, 10 mmoles) and the mixture stirred for 2 hr. A green precipitate was filtered off and washed on the filter with ethanol. The crude product was recrystallised from ethanol (175 ml). Yield, 0.81 g (26%).

$CuBr_2(IT)_2$. This was obtained analogously to the chloride complex, using $CuBr_2$ (4.47 g in 250 ml, 20 mmoles) and isothiazole (6.81 g in 25 ml, 80 mmoles). The product was recrystallised from propanol (650 ml). The yellowish brown complex was vacuum-dried over NaOH. Yield, 2.90 g (36.8%).

$Cu(NO_3)_2(IT)_4$. Isothiazole (13.66 g, 160 mmoles) was added to a methanolic solution of $Cu(NO_3)_2 . 3H_2O$ (4.83 g in 150 ml, 20 mmoles) and the mixture stirred for 2 hr. The violet precipitate was filtered off and recrystallised from methanol (100 ml) containing isothiazole. Yield, 8.20 g (38.8%).

$Cu(NO_3)_2(IT)_2$. Alcoholic solutions of $Cu(NO_3)_2 . 3H_2O$ (4.83 g in 100 ml, 20 mmoles) and isothiazole (6.81 g in 25 ml, 80 mmoles) were mixed and stirred for 2 hr. The precipitate was filtered off, washed on the filter with 3×5 ml portions of ethanol, and vacuum-dried over NaOH. On recrystallising twice from propanol, blue needles were obtained. Yield, 2.34 g (32.7%).

The infrared spectrum of the product before recrystallisation was superimposable on that of $Cu(NO_3)_2(IT)_4$. When ethanol was used as solvent for recrystallisation, an unstable isothiazolium salt formed (i.r. band at 2925 s, br cm^{-1} due to N–H$^+$). Analyses of this compound indicated the composition to be $(ITH)_2[Cu(IT)_2EtO(NO_3)_3]$.

$Cu(ClO_4)_2(IT)_4$. An alcoholic solution of isothiazole 3.41 g in 75 ml, 10 mmoles) was added to an

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[1] W.J. Eilbeck, F. Holmes, and A.E. Underhill, *J. Chem. Soc.* (A), 757 (1967)

[2] J.A. Weaver, P. Hambright, P.T. Talbert, E. Kang, and A.N. Thorpe, *Inorg. Chem.*, 9, 268 (1970).

[3] B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

Table I. Analyses and some physical properties of complexes

Complex	Color	Found (%)				Calculated (%)				μ_{eff}[a] (BM)	Molar Conductivity[b] (mho cm^2 mol^{-1})
		C	H	N	M	C	H	N	M		
$CuCl_2(IT)_2$	Green	24.2	2.1	9.2	—	23.6	2.0	9.2	—	1.93	—
$CuBr_2(IT)_2$	Yellow-brown	18.1	1.4	6.9	—	18.3	1.5	7.1	—	1.96	—
$Cu(NO_3)_2(IT)_4$	Violet	26.7	2.3	15.5	11.6	27.3	2.3	15.9	12.0	1.95	12.6
$(ITH)_2[Cu(IT)_2C_2H_5O(NO_3)_3]$	Violet	27.5	2.4	15.8	10.4	26.4	3.0	15.4	10.0	—	—
$Cu(NO_3)_2(IT)_2$	Blue	20.5	1.8	15.3	17.1	20.1	1.7	15.7	17.8	1.95	11.2
$Cu(ClO_4)_2(IT)_4$	Violet	23.4	2.3	8.6	10.6	23.9	2.0	9.3	10.5	1.96	203
$NiCl_2(IT)_4$	Green	30.2	2.7	11.6	—	30.7	2.6	11.9	—	3.25	—
$NiBr_2(IT)_2$	Yellow	18.5	1.6	7.2	—	18.9	1.8	7.2	—	3.29	—
$Ni(ClO_4)_2(IT)_6$	Pale blue	27.7	2.6	10.9	—	28.1	2.4	10.9	—	3.59	209
$CoCl_2(IT)_2$	Mauve	24.2	2.3	9.4	—	24.0	2.0	9.3	—	5.35	—
$CoBr_2(IT)_2$	Mauve	18.4	1.7	7.1	—	18.5	1.6	7.2	—	5.36	—
$Co(ClO_4)_2(IT)_6$	Rose	28.0	2.5	10.9	—	28.1	2.4	10.9	—	5.00	202
trans-$Co(NCS)_2(IT)_4$	Pink	33.1	2.6	16.6	—	32.6	2.4	16.3	—	5.16	—
cis-$PtCl_2(IT)_2$	Yellow	16.8	1.5	6.6	44.4	16.5	1.4	6.4	44.7	—	—

[a] Measured at room temperature and corrected for diamagnetism. [b]e Masured in $10^{-3}M$ nitromethane solution at 25°, k = 2.51.

Table II. Principal infrared bands of isothiazole complexes (cm^{-1})

$M(Hal)_2(IT)_2$ (M=Cu, Co; Hal=Cl, Br) and $NiBr_2(IT)_2$: 3110 - 3060 w (three bands), 1407±2s, 1403±2sh, 1239±2s, 1233±3s, 1055±3m, 902±4s, 856+5s, 774+4s, 736+4vs.

$Cu(NO_3)_2(IT)_2$: 3138m, 3104m, 3084sh, 1484*s,br, 1458s,br, 1415s, 1304m, 1282*s, 1250vs, 1079m, 1073m, 1034s, 1011*s, 888m, 858s, 809*s, 770s, 753vs, 744vs.

$Cu(NO_3)_2(IT)_4$: 3112m, 3090m, 3070m, 1501sh, 1485*s, 1458s, br, 1411vs,br, 1385*vs,br, 1319*vs,br, 1302*vs, 1279vs,br, 1241 vs, 1063m, 1046s, 1010*m, 911s, 853s, 850s, 820*s, 806*m, 779vs, 762vs, 746vs.

$Cu(ClO_4)_2(IT)_4$: 3125sh, 3090s, 1412vs, 1306m, 1249s, 1245s, 1144sh, 1121*vs,br, 1083sh, 1074*vs, 1047*vs, 935*m, 906vs, 852s, 777s, 764s, 738vs.

$M(ClO_4)_2(IT)_6$(M=Ni, Co): 3090 - 3125m (three bands), 1411±1vs, 1387m, 1302±2m, 1235vs, 1094*vs,br, 1054±2* s,sh, 931±1*w, 894±2s, 845±1vs, 760vs, 752vs, 622vs.

$NiCl_2(IT)_4$: 3078 - 3110m (three bands), 1484m, 1409vs, 1308s, 1236vs, 1073s, 1051s, 891vs, 878m, 837vs, 758s, 736sh, 734vs.

trans-$Co(NCS)_2(IT)_4$: 3105sh, 3085m,br, 2108*s, 2070*vs, 2015*sh, 1483m, 1404vs, 1301m, 1241vs, 1236sh, 1071m, 1054 m, 890vs, 842vs, 817m, 761vs, 734vs, 644m.

cis-$PtCl_2(IT)_2$: 3114m, 3092m, 3070m, 1416vs, 1311s, 1250s, 1236m, 1078m, 1071m, 1050m, 931m, 926m, 843m, 768m, 751s.

* Bands due to the nitrate, perchlorate, or thiocyanate groups.

Table III. X-ray Diffraction Data, Principal d-Spacings

Metal Complex	d-Spacing (Å)							
$CuCl_2(IT)_2$	8.50	7.52		5.38	3.88	3.35	2.98	2.39
$CoCl_2(IT)_2$	8.67	7.53		5.38	3.97	3.19		
$CuBr_2(IT)_2$	8.80	7.55	5.89		3.90	3.57	2.80	2.39
$NiBr_2(IT)_2$	8.80	7.61	6.01		3.96			
$CoBr_2(IT)_2$	8.80	7.62	6.04		3.98		2.89	
$NiCl_2(IT)_4$		7.05	6.33	5.69	3.78		2.83	
$Cu(NO_3)_2(IT)_2$	8.43		6.06	4.77	4.43	3.94		
$Cu(NO)_3)_2(IT)_4$	8.41	7.90	6.45	6.12	4.03	3.63		2.25
$Cu(ClO_4)_2(IT)_4$	7.98	7.23	6.82	6.29	4.50	4.09	3.99	
$Ni(ClO_4)_2(IT)_6$	8.84		5.96	5.12	4.04	3.89		
$Co(ClO_4)_2(IT)_6$	8.90		5.98	5.15	4.04	3.90		
trans-$[Co(NCS)_2(IT)_4]$	8.16	6.90	6.41	4.59	4.34	4.19	3.75	
cis-$[PtCl_2(IT)_2]$	7.23	6.90		5.84	4.71	4.65	3.88	

alcoholic solution of $Cu(ClO_4)_2 . 6H_2O$ (3.71 g in 75 ml, 10 mmoles) and the mixture stirred for 2 hr. The violet product was filtered off and recrystallised from ethanol. Yield, 1.90 g (31.5%).

$NiCl_2(IT)_4$. Alcoholic solutions of $NiCl_2 . 6H_2O$ (2.38 g in 100 ml, 10 mmoles) and isothiazole (1.70 g in 10 ml, 20 mmoles) were mixed and stirred for 1 hr. The green precipitate was filtered off and washed with 3×5 ml portions of alcohol. Yield, 1.22 g (26.0%).

$NiBr_2(IT)_2$. This was isolated from alcoholic solution as described above for the chloride complex, using $NiBr_2 . 3H_2O$ (4.98 g in 40 ml, 18.3 mmoles) and isothiazole (3.21 g, 37.7 mmoles). The yellow product was washed with 4×5 ml portions of alcohol, followed by hexane. Yield, 1.42 g (20.0%).

$Ni(ClO_4)_2(IT)_6$. 2,2–dimethoxypropane (20 ml) was added to an alcoholic solution of $Ni(ClO_4)_2 . 6H_2O$ (3.66 g in 45 ml, 10 mmoles) and the mixture refluxed for 1.5 hr. An alcoholic solution of isothiazole (3.41 g in 10 ml, 40 mmoles) was then added and the mixture refluxed for 24 hr. After cooling to room temperature the pale blue product was filtered off. It was washed quickly with 3×5 ml portions of alcohol and vacuum-dried over NaOH. Yield, 1.05 g (13.7 per cent).

$CoCl_2(IT)_2$. Propanol solutions of $CoCl_2 . 6H_2O$ (2.38 g in 150 ml, 10 mmoles) and isothiazole (3.41 g in 25 ml, 40 mmoles) were mixed and stirred for 2 hr. The mauve precipitate was filtered off and washed quickly with 3×5 ml portions of propanol, followed by hexane. Yield, 2.58 g (79.1%).

$CoBr_2(IT)_2$. This mauve compound was prepared analogously to the chloride complex, using $CoBr_2$ (2.19 g in 400 ml, 10 mmoles) and isothiazole (3.41 g in 15 ml, 40 mmoles). Yield 2.00 g (51.4%).

$Co(ClO_4)_2(IT)_6$. 2,2–dimethoxypropane (15 ml) was added to a butanol solution of $Co(ClO_4)_2 . 2H_2O$ (3.66 g in 30 ml, 10 mmoles). After refluxing for 1 hr isothiazole (5.11 g, 60 mmoles) was added, and the mixture refluxed for another hour. A rose pro-

duct precipitated. After cooling the mixture in an ice bath for 1 hr. The product was filtered off, washed with 4×10 ml portions of acetone and vacuum-dried over drierite. Yield, 4.56 g (59.3%).

Trans$_4$–*Co(NCS)$_2$(IT)$_4$*. Alcoholic solutions of $Co(SCN)_2$ (1.75 g in 125 ml, 10 mmoles) and isothiazole (3.41 g in 10 ml, 40 mmoles) were mixed and stirred for 2 hr. The pink precipitate was filtered off, washed with 3×5 ml portions of ethanol followed by hexane. Yield, 1.91 g (37.0%).

This complex was also prepared using aqueous solutions of $CoCl_2 \cdot 6H_2O$, KSCN, and isothiazole.

Reaction of trans–*Co(NCS)$_2$(IT)$_4$ with α,α'–bipyridyl.* A methanolic solution of α,α'–bipyridyl (0.63 g in 50 ml, 4 mmoles) was added to a methanolic solution of *trans*–$Co(NCS)_2(IT)_4$ (0.98 g in 10 ml, 2 mmoles) and the mixture was stirred for 2 hr. The precipitate was filtered off and washed thoroughly with methanol. Yield, 0.67 g (68.7%).

The infrared spectrum in the 4000 250 cm^{-1} region and X-ray powder pattern of the product were the same as that of *trans*–$Co(NCS)_2(bipy)_2$.[4]

Cis–*PtCl$_2$(IT)$_2$*. This was prepared by a procedure modified from that reported for the corresponding pyridine complex.[5] A solution of isothiazole (0.85 g in 45 ml, 10 mmoles) was added to a solution of $K_2[PtCl_4]$ (2.08 g in 25 ml, 5 mmoles) and the mixture stirred for 24 hr. The cooled mixture was then kept in a refrigerator for 24 hr. The yellow precipitate was filtered off, washed repeatedly on the filter with cold water, and vacuum-dried over NaOH. Yield, 1.76 g (80.7%).

Results and Discussion

Isothiazole and thiazole (pK$_a$ 2.7)[6] may be formally regarded as being derived from pyrazole (pK$_a$ 2.47) and imidazole (pK$_a$ 7.0), respectively, by replacing NH by S. A true spectrum of isothiazole in basic aqueous media could not be obtained hampering the determination of its pK$_a$ of isothiazole by spectrophotometric methods. Its pK$_a$ would, however, be expected to be somewhat less than that of pyrazole. Also, isothiazole forms a series of well-defined complexes with certain transition metal ions (Table I). These complexes were readily prepared from the reaction of an alcoholic solution of isothiazole with an alcoholic solution of the hydrated or anhydrous (prepared in *situ* using 2,2–dimethoxypropane) metal salts. The maximum number of organic ligands coordinated depends primarily on the anion present, and not the stoichiometry of the reactants. In the complexes examined the maximum number of coordinated isothiazoles molecules is found to be six in the perchlorate complexes of nickel(II) and cobalt(II), but for copper(II) the maximum is four, found in the nitrate and perchlorate complexes.

Complexes of MHal$_2$ with Isothiazole. Thiazole gives complexes with metal halides in which the anion is coordinated and may also act as a bridging atom. This has been attributed to the decreased basicity and better π-acceptor characteristics of thiazole compared with pyridine, imidazole, and ammonia.[1] It is not unexpected that isothiazole forms complexes of the type $MHal_2(IT)_2$ ($M = Cu^{II}$, Co^{II}; Hal = Cl, Br) and $NiBr_2(IT)_2$. These complexes probably are polymeric octahedral with halogen bridges and isothiazole in the trans positions. Similar thiazole complexes with copper(II) and cobalt(II) chlorides have been reported.[1] The room-temperature magnetic moments of the cobalt complexes (5.35 (Cl) and 5.36 (Br) BM) are slightly higher than those expected for high-spin octahedral cobalt(II) complexes.[7] The magnetic moments of the copper(II) chloride and bromide complexes are normal, and $NiBr_2(IT)_2$ has a value of 3.29 BM, consistent with an octahedral structure. The X-ray powder patterns of these complexes indicate that the chloride and bromide complexes form two isomorphous categories, and it can be concluded that they are all distorted octahedral complexes with halogen bridges. Silver nitrate precipitated the silver halide from methanol solutions of the complexes, but the residual reactivity of the hetero sulfur atom could not be confirmed.

Nickel(II) chloride gave a complex of composition $NiCl_2(IT)_4$. This complex is octahedral, having a magnetic moment of 3,25 BM, and is similar to the corresponding thiazole complex.[1] The X-ray powder pattern shows that it is quite different structurally from the other halide complexes.

It was not possible to isolate complexes using copper(II), cobalt(II), and nickel(II) iodides.

The complex $PtCl_2(IT)_2$ was prepared in a manner similar to the corresponding pyridine[5] and thiazole[2] complexes. This complex is presumed to be analogous to the pyridine and thiazole complexes with a *cis*-planar configuration and coordination through the nitrogen. The complex was soluble in boiling aqueous isothiazole, but attempts to isolate either *trans*–$PtCl_2(IT)_2$ or $PtCl_2(IT)_4$ were not successful; the analogous complex *cis*–$PtCl_2Py_2$ can easily be converted to *trans*–$PtCl_2Py_2$ and $PtCl_2Py_4$ by this technique.[5]

Copper(II) Nitrate Complexes. Two copper(II) nitrate complexes, $Cu(NO_3)_2(IT)_4$ and $Cu(NO_3)_2(IT)_2$ have been prepared. Two moles of isothiazole were expelled from the former to give the latter by recrystallisation from propanol. The bands due to the nitrate ion in the infrared spectrum of $Cu(NO_3)_2(IT)_2$ can be found by comparison with the spectra of the halide complexes. The free nitrate ion belongs to the symmetry point group D_{3h} and has bands at 1390 (ν_3), 832 (ν_2), and 720 (ν_4) cm^{-1}.[8] In the complex, bands were observed at 1485 (ν_4), 1282 (ν_1), 1011 (ν_2), and 809 (ν_6) cm^{-1}. The ν_3 and ν_5 bands could not be located with certainty. The band at 1011 (ν_2) cm^{-1} and the position of the other bands infer that the nitrate group has a lower symmetry of C_{2v} and is covalently bound to the copper. If the nitrate group acts as a bidentate ligand, the complex would be octa-

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(4) K.K. Ramaswamy and R.A. Krause, *Inorg. Chem.*, 9, 2649 (1970).
(5) G.B. Kauffman, *Inorg. Synth.*, 7, 249 (1963).
(6) A. Albert, R. Goodacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948).
(7) B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 6, 37 (1964)
(8) C.C. Addison and N. Logan, *Adv. Inorg. Radiochem.*, 6, 89 (1964).

hedral. In the complex $Cu(NO_3)_2(IT)_4$ the assignment of bands is more complicated. Bands at 1485 (ν_4), 1319 (ν_1), 1010 (ν_2) and 806 (ν_6) cm^{-1} are similar to those observed in $Cu(NO_3)_2(IT)_2$ and indicate ligand nitrate groups bound to the copper, whereas the bands at 1385 (ν_3), 1302, 1279 (the latter two are shoulders on the band at 1319 cm^{-1}) and 820 (ν_2) cm^{-1} indicate free nitrate ion. Both the complexes have an unassigned band at 1458 cm^{-1}. The magnitude of the difference between ν_4 and ν_1 ($\Delta\nu$), 202 cm^{-1} in $Cu(NO_3)_2(IT)_2$ and 165 cm^{-1} in $Cu(NO_3)_2(IT)_4$, is in the range observed for complexes containing the nitrate group as a ligand.[8,9] The value of $\Delta\nu$ for $Cu(NO_3)_2Py_2$ is 100 cm^{-1}, and $\Delta\nu$ has been suggested to be a function of the covalency of the metal oxygen bond. This data suggests that the complex $Cu(NO_3)_2(IT)_4$ contains both covalent and free nitrate ion. The molar conductivities of both complexes in nitromethane are relatively low, analogous to the corresponding pyridine complex.[10]

Perchlorate Complexes. The three complexes have molar conductivities of about 200 mho cm^2 mol^{-1} in nitromethane, indicating that they are all 1:2 electrolytes in this solvent.[11]

The complexes $M(ClO_4)_2(IT)_6$ ($M = Ni^{II}, Co^{II}$) contain octahedrally coordinated metal ion and free perchlorate ion in the solid state. In the infrared spectrum the strong band occurring at 1094 with shoulder at 1054 ± 2 cm^{-1} in these complexes can be attributed to ionic perchlorate with T_d symmetry.[12] The magnetic moments of 3.59 (Ni) and 5.00 (Co) BM are consistent with an octahedral coordination around the metal ion, although the value for the nickel complex is somewhat higher than is normally observed. The X-ray powder patterns of these two complexes show them to be isomorphous.

It is not possible to predict the environment of the metal atom in $Cu(ClO_4)_2(IT)_4$. The magnetic moment is normal. The strong infrared bands of the perchlorate group at 1121, 1074, and 1047 cm^{-1} suggest that the perchlorate group is acting as a bidentate ligand.[12]

Trans–*Co(NCS)₂(IT)₄*. The ligand exchange reaction of this complex, prepared from $Co(NCS)_2$ and isothiazole, with α,α′–bipyridyl gave *trans*–$Co(NCS)_2(bipy)_2$. Hence it can be assumed that in $Co(NCS)_2(IT)_4$ the two NCS groups are *trans*, and the cobalt is surrounded octahedrally by six nitrogen atoms. The magnetic moment of 5.16 BM is also consistent with octahedral coordination around the cobalt.

The results obtained using isothiazole as a ligand strongly suggest that it has properties similar to thiazole[1] or substituted thiazole,[2] and that coordination occurs through the nitrogen, rather than the sulfur, atom.

Note added in proof. Since the submission of this manuscript the preparation of various isothiazole complexes of cobalt(II) has been described, and it is concluded from the spectral properties that the ligand is N bonded.[13]

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[9] E.J. Duff, M.M. Hughes, and K J. Rutt, *J. Chem. Soc.*, (A), 2126 (1969).

[10] R.V. Biagetti, W.G. Bottjer, and H.M. Heandler, *Inorg. Chem.*, *5*, 379 (1966).

[11] R. Driver and W.R. Walker, *Aust. J. Chem.*, *21*, 331 (1968).

[12] B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[13] R. Rivest and A. Weisz, *Canad. J. Chem.*, *49*, 1750 (1971).