Synthesis and Characterization of Cobalt(III) and Cobalt(IV) Complexes of *N*-(2-Hydroxyphenyl)salicylamide and Homologues†

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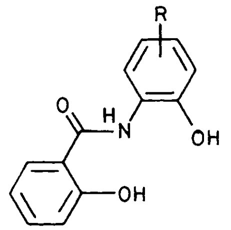
Tridentate trianionic chelating ligands, *N*-(2-hydroxyphenyl)salicylamide (H_3L^1) and its homologues with a substituent on the 2-hydroxyphenyl moiety (5-Me, H_3L^2; 5-Cl, H_3L^3; 4-NO_2, H_3L^4; 5-NO_2, H_3L^5), were utilized for the synthesis of cobalt complexes. The ligands H_3L^1 and H_3L^2 gave uncharacterized substances when treated with a cobalt(II) salt, whereas H_3L^3—H_3L^5 formed cobalt(III) complexes of general formula $K_3[CoL_2]$. The cobalt(III) complexes were characterized by elemental analyses, thermogravimetric analyses, electronic spectra, and cyclic voltammograms. Cyclic voltammograms showed two redox couples at significantly low potential, which were assigned to the Co^{IV}–Co^{III} and Co^{V}–Co^{IV} redox processes based on controlled-potential electrolysis and e.s.r. investigations. The cobalt(III) complexes were readily oxidized chemically (with I_2) or electrochemically to the cobalt(IV) complexes, which were identified by an e.s.r. signal near g = 2.0 with an eight-line hyperfine structure ($A_{av.}$ = 0.001 92 cm^{-1}).

There is growing interest in the co-ordination chemistry of metal ions in unusual, high oxidation states because of the novel physiochemical properties and reactivities expected for such complexes.[1] Most suitable known ligands are highly electronegative, inorganic ions such as O^{2-}, F^-, or Cl^-, but the variety of metal complexes derived from those inorganic ions is very limited. In order to develop this co-ordination chemistry, new organic ligands of various types must be exploited. The prerequisites for the ligands are (1) resistance to the high oxidizing power of metal ions and (2) strong donating ability to satisfy the high Lewis acidity of metal ions. Recent investigations have revealed that the deprotonated nitrogen of organic amides[2–4] or deprotonated oxygen of phenols[5] donates (in both σ and π manners) to metal ions, stabilizing high oxidation states. Hence, polyanionic chelating ligands comprising amide and phenolic or alcoholic groups have been developed.[6–9] Quadridentate ligands such as 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane[6] and 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene[7] were first utilized by Collins and co-workers to synthesize cobalt(IV) and osmium(IV) complexes. Similar tridentate ligands *N*-(2-hydroxyphenyl)salicylamide and homologues were developed in our laboratory, and form stable manganese(IV) and fairly stable manganese(V) complexes of general formulae $[MnL_2]^{2-}$ and $[MnL_2]^-$. As far as we know the latter is the first manganese(V) complex with organic ligands.

Compared with manganese ion, higher oxidation states (4+ and 5+) of cobalt ion are much harder to attain,[1b] and only a few cobalt(IV) complexes of halide or oxide ion are known.[10–12] Formally Co^{4+} is present in the complexes of *o*-phenylenediamine dianion[13,14] and 1,2-bis(trifluoromethyl)-1,2-dithiolate,[15] but they should be ascribed to ligand-centred cation radicals. There are some reports on the detection of cobalt(IV) species by electrochemical methods[16] and e.s.r. spectroscopy.[17] However, characterized cobalt(IV) complexes co-ordinated to organic ligands are still very limited.[7,16–18] In view of these facts and as an extension of our previous study, we have carried out an investigation on cobalt complexes using *N*-(2-hydroxyphenyl)salicylamide and its homologues in the hope of obtaining cobalt complexes of higher oxidation states. This paper reports the synthesis, characterization, and properties of cobalt(III) and cobalt(IV) complexes, $[CoL_2]^{3-}$ and $[CoL_2]^{2-}$.



	R
H_3L^1	H
H_3L^2	5-Me
H_3L^3	5-Cl
H_3L^4	4-NO_2
H_3L^5	5-NO_2

Experimental

Preparations.—The ligands were obtained by the method described previously.[9]

$K_3[CoL_2]$ (L = L^3—L^5). The complexes were obtained by similar methods. That of L^3 is described. A methanol–water solution (1:1, 20 cm^3) containing H_3L^3 (527 mg), KOH (300 mg), and cobalt(II) acetate tetrahydrate (250 mg) was stirred overnight at ambient temperature. The brown precipitate was collected by suction filtration and crystallized from absolute methanol as reddish brown microcrystals. The yield after recrystallization was 285 mg.

The L^4 and L^5 complexes formed deep reddish brown microcrystals.

Measurements.—Analytical data for C, H, and N were obtained at the Elemental Analysis Service Center, Kyushu

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† *Non-S.I. unit employed*: G = 10^{-4} T.

Table 1. Elemental analyses and electronic spectral data of cobalt complexes

	Analysis^a/%					$\lambda_{max.}/10^3$ cm^{-1}(log ε/dm^3 mol^{-1} cm^{-1})^b		
Complex	C	H	N	H_2O^c	Co^d			
$K_3[CoL^3_2]\cdot 5H_2O$	44.75 (45.25)	2.45 (2.65)	4.05 (4.05)	13.6 (13.4)	6.7 (7.3)	16.9(2.90)	23(sh)($\approx$3.4)	29.2(4.20)
$K_3[CoL^4_2]\cdot 4H_2O$	45.50 (45.05)	2.65 (2.35)	7.85 (8.10)	8.8 (9.1)	8.3 (7.5)	16(sh)($\approx$2.1)	21.0(4.29)	30.1(4.42)
$K_3[CoL^5_2]\cdot 5H_2O$	43.95 (43.90)	2.86 (2.55)	7.75 (7.85)	12.2 (11.1)	7.9 (7.3)	16(sh)($\approx$2.1)	22.6(4.26)	29.8(4.39)
$K_2[CoL^3_2]$						18.5(2.85)		28.6(4.05)

^{a} Calculated values in parentheses. ^{b} In methanol. ^{c} Determined by thermogravimetric analysis. ^{d} Determined by atomic absorption spectrometry.

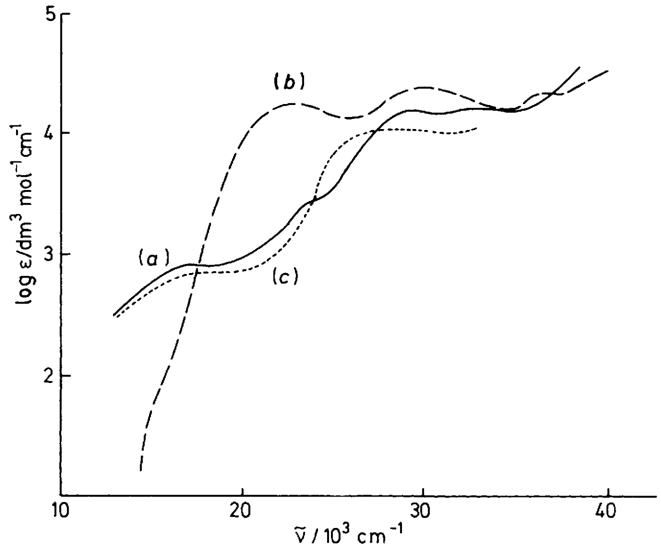

Figure 1. Electronic spectra in methanol: (a) $K_3[CoL^3_2]$; (b) $K_3[CoL^4_2]$; (c) cobalt(IV) complex of L^3 obtained by electrochemical oxidation at +0.03 V

University. Cobalt was analyzed on a Nippon Jarrel-Ash AA781 atomic absorption and flame emission spectrophotometer. Thermogravimetric analyses were carried out on a Rigaku TG instrument. Infrared spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls, electronic spectra on a Shimadzu model MPS-5000 Multipurpose spectrophotometer in methanol, X-band e.s.r. spectra in frozen dichloromethane solutions at liquid-nitrogen temperature on a JES-ME-3 spectrometer. Cyclic voltammograms were obtained on a Yanagimoto P-1000 voltammetric analyzer in dichloromethane containing tetraethylammonium tetrafluoroborate (0.1 mol dm^{-3}) as the supporting electrolyte. Measurements were carried out using a three-electrode cell equipped with a glassy carbon working electrode, a platinum coil auxiliary electrode, and a calomel electrode as the reference.

Results and Discussion

Synthesis and Characterization of Cobalt(III) *Complexes*.—All the cobalt(III) complexes synthesized in this study are stable in air. Analytical results are given in Table 1. The presence of lattice water was evidenced by a broad i.r. band[19] near 3 400 cm^{-1} (measured on Nujol mulls) and evaluated by thermogravimetric analyses (dehydrated at 118—124 °C, see Table 1). Magnetic measurements revealed that all the complexes are diamagnetic, indicating the 3+ oxidation state of the metal ion. All these facts are in accord with the formulation $K_3[CoL_2]\cdot nH_2O$ ($L = L^3$—L^5; $n = 4$—5). (The complexes will be represented without the hydrated water hereafter.) So far all our efforts to synthesize cobalt complexes of H_3L^1 and H_3L^2 were in vain. With these ligands the reaction mixture once formed a deep green solution, but the colour gradually faded and finally uncharacterized and hardly soluble materials separated from the solution.

In methanol the complexes seemed to be stable and the colour of the solution (L^3, dull brown; L^4 and L^5, bright reddish brown) hardly changed on prolonged standing in air. Electronic spectra of the complexes in methanol are shown in Figure 1. The spectra obey Beer's law in the concentration range 1×10^{-3}—1×10^{-4} mol dm^{-3}. The numerical data are summarized in Table 1. The complex $K_3[CoL^3_2]$ shows moderately intense absorption bands at 16.9×10^3 and 23×10^3 cm^{-1} and a very intense band at 29.2×10^3 cm^{-1}. For octahedral cobalt(III) complexes two spin-allowed *d–d* transitions (${}^1T_{1g} \longleftarrow {}^1A_{1g}$ and ${}^1T_{2g} \longleftarrow {}^1A_{1g}$) are expected in the visible region. The bands at 16.9×10^3 and 23×10^3 cm^{-1} found for $K_3[CoL^3_2]$ are, however, too intense to attribute to the spin-allowed *d–d* transition. In fact the lowest band for the L^4 and L^5 complexes is a discernible shoulder around 17×10^3 cm^{-1} and its estimated absorption coefficient is 100 dm^3 mol^{-1} cm^{-1} at best [curve (*b*), Figure 1]. We believe that the moderately intense band at 16.9×10^3 cm^{-1} of the L^3 complex is a charge-transfer (c.t.) band, superposed by the *d–d* bands, though proper assignment of the c.t. band cannot be made in this study. The intense band at 29.2×10^3 cm^{-1} is assigned to an intraligand transition.[9] Such a c.t. band as found for $K_3[CoL^3_2]$ was lacking in the spectra of $K_3[CoL^4_2]$ and $K_3[CoL^5_2]$. Instead, the latter complexes were characterized by an intense absorption near 22×10^3 cm^{-1}. A similar absorption band was observed for manganese(IV) complexes with L^4 and L^5 and attributed to an intraligand transition associated with the nitro-substituent of the ligands.[9]

The complexes are presumed to have a six-co-ordinate structure in the *mer* configuration. We attempted to grow single crystals suitable for X-ray analysis but were not successful.

Electrochemistry.—Electrochemical properties of the complexes were examined by cyclic voltammetry. Each cyclic-voltammogram comprised three irreversible waves at positive potentials and one irreversible wave at a negative potential. The cyclic voltammogram of $K_3[CoL^3_2]$ is shown in Figure 2. The waves are numbered as I—IV from the lowest potential. In this study our attention was focused on waves II and III. When measured in the range from −0.4 to +0.6 V, the cyclic voltammograms showed much improved reversibility (see

Table 2. Electrochemical data[a] and e.s.r. parameters of cobalt complexes

Complex	Co^{III}–Co^{IV} E_{pa}	Co^{III}–Co^{IV} E_{pc}	Co^{III}–Co^{IV} $E_{\frac{1}{2}}$[b]	Co^{IV}–Co^{V} E_{pa}	Co^{IV}–Co^{V} E_{pc}	Co^{IV}–Co^{V} $E_{\frac{1}{2}}$[b]	g_{iso}	g_{iso}	$A_{iso}/10^{-4}$ cm^{-1}	$A_{iso}/10^{-4}$ cm^{-1}
$K_3[CoL^3{}_2]\cdot5H_2O$	0.05	−0.12	−0.04	0.35	0.17	0.26	2.000[c]	2.000[d]	19.4[c]	19.0[d]
$K_3[CoL^4{}_2]\cdot4H_2O$	0.27	0.16	0.22	0.57	—	—	2.001[c]	2.002[d]	20.3[c]	—
$K_3[CoL^5{}_2]\cdot5H_2O$	0.38	0.24	0.31	0.66	—	—	1.999[c]	1.999[d]	—	—

[a] In volt *vs.* s.c.e., scan rate 80 mV s^{-1}. Determined on a glassy carbon electrode in CH_2Cl_2. [b] $E_{\frac{1}{2}} = (E_{pc} + E_{pa})/2$. [c] Chemical oxidation. [d] Electrochemical oxidation.

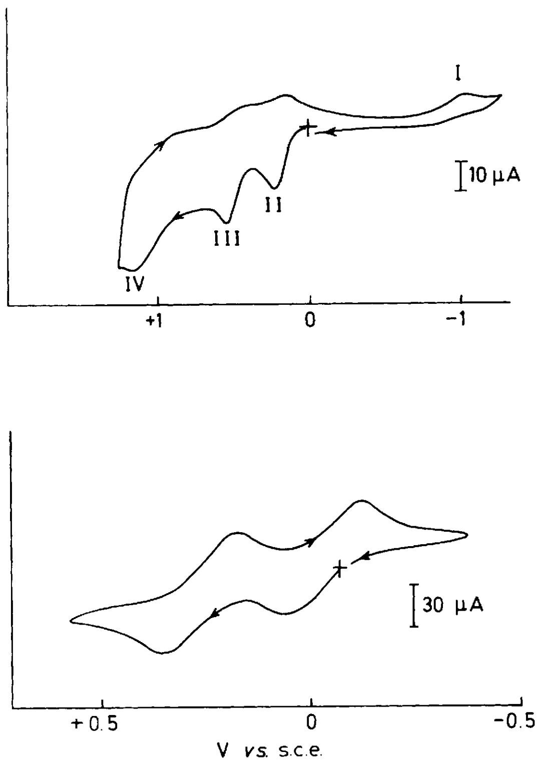

Figure 2. Cyclic voltammograms of $K_3[CoL^3{}_2]$, sweep in the range −1.3 to +1.2 V (above) and in the range −0.4 to +0.6 V (below): glassy carbon electrode, in CH_2Cl_2, scan rate = 80 mV s^{-1}, concentration = *ca.* 1 × 10^{-3} mol dm^{-3}

Figure 2). That is, wave II is pseudo-reversible for all the complexes, judging from the separation between the cathodic and anodic peaks ($\Delta E_p = E_{pc} - E_{pa} = 110$—170 mV). Wave III was also pseudo-reversible for $K_3[CoL^3{}_2]$ but irreversible for $K_3[CoL^4{}_2]$ and $K_3[CoL^5{}_2]$. Controlled-potential electrolysis was carried out for $K_3[CoL^3{}_2]$ near each anodic peak of waves II and III, and the results demonstrated that each of the oxidation processes involves a one-electron transfer. Since the ligands show no electrochemical response up to +1.0 V in methanol containing KOH (0.004 mol dm^{-3}), waves II and III can be attributed to the redox processes at the metal centre, Co^{IV}–Co^{III} and Co^{V}–Co^{IV}. Therefore, wave I at the lowest potential can be assigned to the Co^{III}–Co^{II} redox process. Wave IV at the highest potential must be due to the oxidation at the ligand centre, because the 6+ oxidation state of cobalt is not known. Electrochemical results for the present complexes are summarized in Table 2.

It should be emphasized that the Co^{IV}–Co^{III} potentials of the present complexes are significantly low compared with other cobalt complexes of organic ligands and the $Co^{III} \longrightarrow Co^{IV}$ oxidation of $K_3[CoL^3{}_2]$ occurs even at a negative potential [*vs.* saturated calomel electrode (s.c.e.)]. Further, the Co^{V}–Co^{IV} wave was first recognized in this study. The high stabilization of the 4+ and 5+ oxidation states of cobalt is evidently due to the strong donation of the ligands through the deprotonated amide nitrogen and phenolic oxygens. Both the Co^{IV}–Co^{III} and Co^{V}–Co^{IV} potentials are dependent upon the electronic nature of the substituents on the ligands. Thus, both potentials shift by 180—270 mV to more positive values on going from L^3 to L^5. This trend is the same as that found for the manganese complexes of L^1—L^5 [9] and related Schiff bases[20] where a good linear correlation exists between the redox potentials and Hammett's constants for the substituents. When we take into consideration such a linear correlation, the Co^{IV}–Co^{III} redox processes for the complexes with L^1 and L^2 are expected to occur at −0.35 and −0.41 V, respectively. This implies that these complexes should be oxidized to cobalt(IV) in the presence of molecular oxygen. The fact that the reaction mixtures with L^1 and L^2 formed a deep green solution, which faded finally, is a good indication of the formation of cobalt(IV) species, since such a coloration was also seen when the solution of $K_3[CoL^3{}_2]$ was electrochemically oxidized to the cobalt(IV) species as mentioned below. We believe that the cobalt(IV) complexes of L^1 and L^2 were indeed formed but soon decomposed because the ligands cannot coexist with cobalt(IV) ion.

Cobalt(IV) *Complexes and E.S.R. Spectra.*—The e.s.r. technique is the most useful tool to investigate cobalt(IV) complexes *in situ.*[17] We carried out chemical and electrochemical oxidations of $K_3[CoL_2]$ ($L = L^3$—L^5) in dichloromethane solutions and examined the *X*-band e.s.r. spectra of the resulting cobalt(IV) complexes. When 0.5 mol equivalent of iodine was added to a dichloromethane solution of each cobalt(III) complex the solution became deep purple and showed an e.s.r. signal near $g = 2.0$ at liquid-nitrogen temperature. In particular, a well resolved eight-line hyperfine structure ($A_{av.} = 0.001\ 92$ cm^{-1}) was observed at $g = 2.0$ in the case of the L^3 complex. Such a hyperfine structure is characteristic of the cobalt nucleus ($I = \frac{7}{2}$). When $K_3[CoL^3{}_2]$ was oxidized electrochemically at +0.03 V the solution became deep green and showed practically the same e.s.r. spectrum as that given in Figure 3. E.s.r. spectral results are given in Table 2. The *g* values found for the L^3—L^5 complexes and the isotropic hyperfine coupling constants observed for the L^3 complex are comparable to those reported for a bis(benzamidato)cobalt(IV)[7] and for organobis(dioximato)cobalt(IV) complexes.[17] Thus, the e.s.r. spectral results unambiguously demonstrate that the oxidation occurs at the metal centre to give low-spin cobalt(IV) species. All our efforts to isolate cobalt(IV) complexes were in vain at this stage.

The cobalt(IV) complexes generated electrochemically in solution are sufficiently stable so as to allow electronic spectral measurements. In Figure 1 is included the spectrum of the

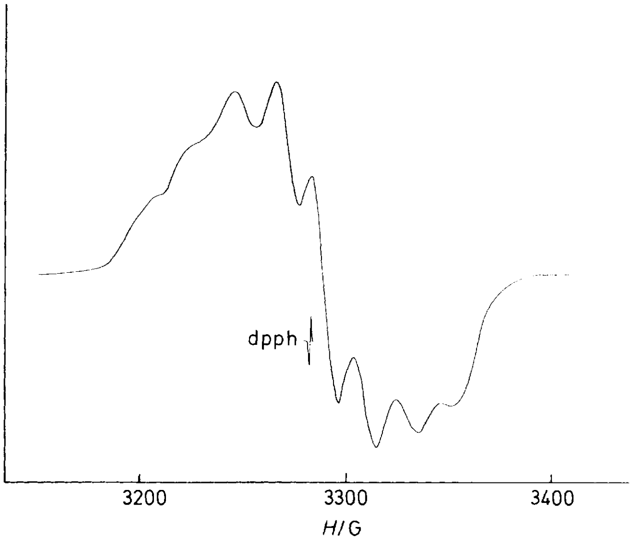

Figure 3. E.s.r. spectrum of L^3–Co^{IV} complex generated by electrochemical oxidation at +0.03 V; dpph = diphenylpicrylhydrazyl

cobalt(IV) complex of L^3, $[CoL^3_2]^{2-}$, which shows a moderately intense absorption band at 18.5×10^3 cm^{-1} and a very intense intraligand band at 28.6×10^3 cm^{-1}. The visible band may be assigned to one of the *d–d* components of low-spin cobalt(IV) (d^5).

Acknowledgements

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References

1 (*a*) W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1972, **7**, 353; (*b*) W. Levason and C. A. McAuliffe, *ibid.*, 1974, **12**, 151; (*c*) D. J. Gulliver and W. Levason, *ibid.*, 1982, **46**, 1.
2 D. W. Margerum, *Pure Appl. Chem.*, 1983, **55**, 23.
3 L. L. Diaddario, W. R. Robinson, and D. W. Margerum, *Inorg. Chem.*, 1983, **22**, 1021.
4 E. Kimura, A. Sakonaka, R. Machida, and M. Kodama, *J. Am. Chem. Soc.*, 1982, **104**, 4255.
5 S. E. Jones, D. Chin, and D. T. Sawyer, *Inorg. Chem.*, 1981, **20**, 4257; D. Chin, D. T. Sawyer, W. P. Schaefer, and C. J. Simmons, *ibid.*, 1983, **22**, 752.
6 J. A. Christie, T. J. Collins, T. E. Krafft, B. D. Santarsiero, and G. H. Spies, *J. Chem. Soc., Chem. Commun.*, 1984, 198.
7 F. C. Anson, T. J. Collins, R. J. Coots, S. L. Gipson, and T. G. Richmond, *J. Am. Chem. Soc.*, 1984, **106**, 5037.
8 T. J. Collins, T. G. Richmond, B. D. Santarsiero, and B. G. R. T. Treco, *J. Am. Chem. Soc.*, 1986, **108**, 2088.
9 M. Koikawa, H. Ōkawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1988, 641.
10 J. W. Quail and G. A. Rivett, *Can. J. Chem.*, 1972, **50**, 2447.
11 R. Sholder, *Angew. Chem.*, 1958, **70**, 583; R. Sholder and W. Klemm, *ibid.*, 1954, **66**, 461.
12 V. M. Z. Jansen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1973, **398**, 54; *ibid.*, 1975, **417**, 35.
13 A. C. Balch and R. H. Holm, *J. Am. Chem. Soc.*, 1966, **88**, 5201.
14 L. F. Warren, *Inorg. Chem.*, 1977, **16**, 2814.
15 A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.
16 I. Levitin, A. L. Sigan, and M. E. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1975, 469; R. H. Magnuson, J. Halpern, I. Y. Levitin, and M. E. Vol'pin, *ibid.*, 1978, 44; J. Halpern, M. S. Chan, T. S. Roche, and G. M. Tom, *Acta Chem. Scand., Ser. A*, 1979, **33**, 141.
17 J. Topich and J. Halpern, *Inorg. Chem.*, 1979, **18**, 1339; J. Halpern, J. Topich, and K. I. Zamaraev, *Inorg. Chim. Acta*, 1976, **20**, L21; J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Am. Chem. Soc.*, 1975, **97**, 1606.
18 B. K. Bower and H. G. Tennent, *J. Am. Chem. Soc.*, 1972, **94**, 2512.
19 P. J. Lucchesi and W. A. Glasson, *J. Am. Chem. Soc.*, 1956, **78**, 1347.
20 H. Ōkawa, M. Nakamura, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 466.

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