that of the macrocyclic tetraamine ligands: these ligands have their donor atoms at the corners of a square. In fact it has been found that the reaction between the copper(II) ion and cyclen (cyclen = 1,4,8,12-tetraazadodecane) has an exceptionally large positive value of $\Delta S°$, viz., 50 cal K^{-1} mol^{-1}.[10] cyclen unlike tach does not have to overcome a conformational energy barrier and therefore its reaction with the copper(II) ion is also accompanied by an appreciably exothermic heat change. Presumably the rigidity of the ligand is crucial to the comparatively high stability in solution of metal complexes with cyclic triamines.[11] The entropy contribution arising from the rigidity of the ligand has been completely ignored up to the present time in interpreting the high stabilities of complexes with macrocycles (the macrocyclic effect).[12]

The reaction of $Zn(tach)^{2+}$ with the OH^- ion, i.e., hydrolysis, both is exothermic and is favored by the entropy change. The exothermicity probably reflects the formation of a stronger metal–oxygen bond following the removal of a proton. Furthermore the reaction leads to a decreased electric charge and this in turn leads to the release of some of the molecules of water of solvation. This clearly explains the positive value of $\Delta S°$. Similar behavior is found in the case of the complex Zn(3,3-tri).[9] Here the hydrolysis is ca. 10 times less favored than in the case of $Zn(tach)^{2+}$ because both the enthalpy and entropy contributions are less favorable.

The thermodynamic behavior of tach toward the proton is also somewhat different from that of linear triamines. The stepwise basicity of tach is less than that of the triamine 3,3-tri which like tach has basic nitrogens separated by propylenic chains.[6] This lower basicity is the result of different entropy and enthalpy contributions. What is more, unlike 2,2-tri[13] and 3,3-tri,[9] for both of which the second step in the protonation is more exothermic than the first, in the case of tach, $-\Delta H°_1 > -\Delta H°_2 > -\Delta H°_3$. The entropy change $\Delta S°$ decreases for each successive step as in the case of the linear triamines and in general for all polyamines.

Experimental Section

cis,cis-tach was prepared and then purified by sublimation according to a method to be reported.[14] The purity of the substance was checked by C, H, and N analyses and pH titrations. A standard KOH solution (∼0.3 M) was prepared by washing KOH pellets repeatedly under nitrogen with carbon dioxide free water.

The solution from the third washing was collected. The normality and purity of the KOH solution were determined by pH titrations following the method of Gran.[15] As the calorimetric apparatus requires more diluted reagents, two solutions of KOH (0.01 and 0.02 M) were obtained by diluting the standard KOH solution with carbon dioxide free water. The titer of the diluted solutions was checked calorimetrically against the neutralization ($H^+ + OH^-$) in 0.1 M KCl; the heat of this reaction (−13.395 ± 0.016 kcal mol^{-1}) has been determined in previous experiments and it is in good agreement with the reported values.[16] An HCl solution was prepared by diluting the azeotropic mixture and the acidity was determined by titration against borax. A solution of $ZnCl_2$ was prepared and the zinc content determined gravimetrically as anthranilate. The tach solution (0.1 M) was prepared by dissolving the ligand in CO_2-free water and was kept under nitrogen. The ligand concentration was determined by pH titrations.

The calorimetric apparatus was an LKB 10700-1 Flow Microcalorimeter. Reagents were injected into the mixing cell by LKB Perpex peristaltic pumps. The design of the experiment and the calibration of the apparatus have already been described in detail.[17] In the protonation measurements a peristaltic pump (pump B) injected a solution of the free ligand tach into the calorimeter; the other pump (pump A) injected an HCl solution. The appropriate H^+:tach ratios were obtained by changing the flow rates of the peristaltic pump and/or preparing solutions of different concentrations.

In the case of metal complex formation measurements, pump A injected a solution containing the ligand tach, an excess of hydrochloric acid, and an appropriate amount of a zinc(II) salt. Pump B was connected to the KOH solutions. All solutions used in the calorimetric experiments were adjusted to the 0.1 ionic strength by KCl, Erba CGS.

The method by which $\Delta H°$ is obtained from the calorimetric data has been described previously.[17] The values of the equilibrium constants β_{pqr} used in the calculations were those reported in ref 4. The ionic product of the water ($K_w = 1.63 \times 10^{-14}$) was taken from ref 16. The calculations were performed with an IBM 360 computer.

Acknowledgment. We thank Professor Gerold Schwarzenbach for having kindly furnished the ligand tach and the Italian CNR for financial support.

Registry No. tach, 26150-46-9; Zn, 7440-66-6.

Supplementary Material Available: Tables II and III listing the experimental details of the calorimetric measurements (analytical molar flow rates of the acid, metal ion and ligand, heat flow values, and percent of the species formed during the experiments) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta, Rev.*, **7**, 43 (1973), and references therein.
(2) C. Bianchini, L. Fabbrizzi, P. Paoletti, and A. B. P. Lever, *Inorg. Chem.*, **14**, 197 (1975).
(3) R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, **90**, 621 (1968).
(4) R. F. Childers, R. A. D. Wentworth, and L. J. Zompa, *Inorg. Chem.*, **10**, 302 (1971).
(5) R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 2403 (1974).
(6) A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, **5**, 1384 (1966).
(7) M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960).
(8) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963); M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).
(9) P. Paoletti, F. Nuzzi, and A. Vacca, *J. Chem. Soc. A*, 1386 (1966).
(10) M. Kodame and E. Kimura, *J. Chem. Soc., Chem. Commun.*, 327 (1975).
(11) M. De Ronde, D. Driscoll, R. Yang, and L. J. Zompa, *Inorg. Nucl. Chem. Lett.*, **11**, 521 (1975).
(12) F. P. Hinz and D. W. Margerum, *J. Am. Chem. Soc.*, **96**, 4993 (1974); *Inorg. Chem.*, **13**, 2941 (1974).
(13) M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961).
(14) H. Egli and G. Schwarzenbach, to be submitted for publication.
(15) G. Gran, *Analyst*, **77**, 661 (1952); F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, **42**, 37 (1965).
(16) H. S. Harned and B. B. Owen "The Physical Chemistry of Electrolytic Solutions", 3d ed, Reinhold Publishing Corporation, New York, N.Y., 1958.
(17) C. Bianchini, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1036 (1975).

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British
Columbia, Canada V6T 1W5

Bis(fluorosulfato)bromonium(III) and -iodonium(III) Cations $[Br(SO_3F)_2]^+$ and $[I(SO_3F)_2]^+$

P. A. Yeats, B. Landa, J. R. Sams, and F. Aubke*

Received September 9, 1975 AIC506710

Iodine and bromine tris(fluorosulfate) have been known for some time[1] together with some of their physical and chemical properties[2,3] and Raman spectra.[4] Also known are the corresponding tetrakis(fluorosulfate) anions of iodine and bromine, e.g., as the potassium salts $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$.[5] Fluorosulfate ion transfer according to

$$KSO_3F + I(SO_3F)_3 \xrightarrow[S_2O_6F_2]{+25\ °C} K[I(SO_3F)_4] \qquad (1)$$

is not only a logical link between both types of compounds but also a useful synthetic route.[4] In this reaction $I(SO_3F)_3$ is found to act as an SO_3F^- ion acceptor.

In analogy to the chemical behavior of some structurally related interhalogen compounds such as ICl_3 and BrF_3, both $I(SO_3F)_3$ and $Br(SO_3F)_3$ may also be expected to act as SO_3F^- ion donors toward suitable acceptors. However, no stable compounds of this type have been reported to date. The same applies to any other oxy acid derivative of trivalent iodine and bromine.

Table I. Mössbauer Spectra at 80 K[a]

Compd	δ, mm/s	Δ, mm/s	Γ, mm/s	Ref
$[I(SO_3F)_2]_2[Sn(SO_3F)_6]$	−0.27	0	1.30	This work
$[Br(SO_3F)_2]_2[Sn(SO_3F)_6]$	−0.23	0	1.29	This work
$Sn(SO_3F)_4 \cdot 2BrSO_3F$	−0.16	0.87	1.29, 1.26	This work
$K_2[Sn(SO_3F)_6]$	−0.26	0	1.14	8
$Cs_2[Sn(SO_3F)_6]$	−0.25	0	1.11	8
$(NO)_2[Sn(SO_3F)_6]$	−0.28	0	1.41	8
$(ClO_2)_2[Sn(SO_3F)_6]$	−0.30	0	1.28	8
$Sn(SO_3F)_4$	−0.27	1.34	1.05, 1.32	9

[a] δ is isomer shift, relative to $BaSnO_3$; Δ is quadrupole splitting; Γ is line width at half-peak height.

Some indications for the existence of stable cations of the type $[Hal(SO_3F)_2]^+$, with Hal = Br or I, may be found in the literature. The observed high specific conductances of the halogentris(fluorosulfates)[3] have been interpreted in terms of self-ionization equilibria of the type

$$2Hal(SO_3F)_3 = [Hal(SO_3F)_2]^+ + [Hal(SO_3F)_4]^- \quad (Hal = Br \text{ or } I) \qquad (2)$$

The solution behavior of $I(SO_3F)_3$ in HSO_3F[6] has been described as "ampholytic" with the solute capable of acting as acid or as base. Basic behavior may involve $[I(SO_3F)_2]^+$. The corresponding cation $[Br(SO_3F)_2]^+$ has been identified tentatively in superacid solution by conductometry and a limited number of vibrational bands.[7]

The recent synthesis and identification of complexes containing the anion $[Sn(SO_3F)_6]^{2-}$ [8] by Raman and ^{119}Tin Mössbauer spectroscopy indicated that the use of $Sn(SO_3F)_4$[9] may lead to SO_3F^- abstraction from $I(SO_3F)_3$ or $Br(SO_3F)_3$. In particular ^{119}Sn Mössbauer spectra should allow the detection of the complex anion.

Discussion

Two different routes were used to synthesize the desired complexes. $[I(SO_3F)_2]_2[Sn(SO_3F)_6]$ was formed when stoichiometric amounts of $I(SO_3F)_3$ and $Sn(SO_3F)_4$ were allowed to react first for 3 days at room temperature with peroxydisulfuryl difluoride as solvent and then without solvent at +50 °C for 1 more day.

The corresponding bromine compound was obtained by first dissolving a known amount of $Sn(SO_3F)_4$ in an excess of $BrSO_3F$. From the resulting black-brown solution the excess $BrSO_3F$ was removed in vacuo until a brown slightly inhomogenous solid of the approximate composition $2BrSO_3F \cdot Sn(SO_3F)_4$ was obtained. The solid material was subsequently oxidized with $S_2O_6F_2$ to the desired product according to

$$2BrSO_3F \cdot Sn(SO_3F)_4 + 2S_2O_6F_2 \rightarrow [Br(SO_3F)_2]_2[Sn(SO_3F)_6] \qquad (3)$$

Both compounds were light yellow-white, hygroscopic solids. Their decomposition points were slightly lower than those of $(NO)_2[Sn(SO_3F)_6]$ or $(ClO_2)_2[Sn(SO_3F)_6]$.[8]

The presence of the $[Sn(SO_3F)_6]^{2-}$ ion in both new complexes is most evident from the ^{119}Sn Mössbauer data, listed in Table I. As for the previously reported hexakis(fluorosulfato)stannates[8] only single-line spectra are obtained with isomer shifts at −0.25 to −0.30 mm/s relative to $BaSnO_3$. The absence of any resolvable quadrupole splitting suggests a spherical charge distribution around tin, consistent with an octahedral environment. The relatively large line width values however may be due to some unresolved quadrupole splitting. As for $(NO)_2[Sn(SO_3F)_6]$ and the corresponding ClO_2^+ complex, a distortion of the octahedral environment may be responsible for the large Γ values.

The intermediate of the composition $2BrSO_3F \cdot Sn(SO_3F)_4$ shows Mössbauer parameters consistent with the formulation as a coordination complex between $BrSO_3F$ and $Sn(SO_3F)_4$, presumably via bridging SO_3F– groups. Unfortunately, due to the dark brown color, we were unable to obtain Raman spectra of this rather interesting product.

Table II. Raman Data (cm^{-1})[a]

$[I(SO_3F)_2]_2$-$[Sn(SO_3F)_6]$	$[Br(SO_3F)_2]_2$-$[Sn(SO_3F)_6]$	$K_2[Sn(SO_3F)_6]$[b]
1445 w	1500 ms	
1430	1487 mw, sh	
1412 mw	1420 mw	1407 m
1382 ms	1387 ms	1390 m
1368		
1253 vs	1248 s	
		1278 ms
1213 s		
1183 s	1197 s	1228 m
1133 vw	1145 s	1208 m
1103 vs	1092 s	1096 s
1012 m	1020 ms	1002 m
963 vs	985 m	
911 vw		
883 s	865 vs	
		859 m
857 vw	850 m, sh	836 m
828 m	830 w	823 m
712 m	745 s	
690 m		
663 vs	652 vs	
650 s	640 s	
628 ms	n.o.	625 s
577 m	596 mw	582 m
561 m	558 m	560 m
548 mw	530 m	
530 vw		
455 ms	464 s	
431 w	430 vw, sh	435 m
410 m	414 ms	416 m
369 w	386 m	360 m
358 w		
329 ms		
	309 s	
284 ms		
254 ms	264 ms	266 s

[a] Key: w, weak; m, medium; s, strong; v, very; sh, shoulder; n.o., not observed. [b] Reference 8.

As was to be expected, the vibrational spectra for both new hexakis(fluorsulfato)stannates are rather complex. The observed Raman shifts for both compounds are listed in Table II. Due to the reactive nature of the compounds, only poorly resolved ir spectra down to 800 cm^{-1} (BaF_2 windows) could be obtained.

Due to extensive overlap of absorption bands, in particular, in the fluorosulfate deformation range, a complete assignment of the observed bands appears impossible but a few comments may be safely made. As can be seen from the listed frequencies for $K_2[Sn(SO_3F)_6]$, the Raman spectra for the two new complexes are consistent with the presence of the $[Sn(SO_3F)_6]^{2-}$ ion. Additional frequencies in the SO and SF stretching range may be assigned to $\nu(SO_2)_{as}$ at 1440–1500 cm^{-1}, $\nu(SO_2)_s$ at ~1250 cm^{-1}, ν(SO(Hal)) at ~970 cm^{-1}, and ν(SF) at −870 cm^{-1}. These assignments are consistent with a monodentate, somewhat polarized $-OSO_2F$ group bonded to iodine or bromine, respectively.

Similar band positions are found for the $-OSO_2F$ group in the anions $[I(SO_3F)_4]^-$ and $[Br(SO_3F)_4]^-$, but they are generally lowered by 20–40 cm^{-1}. However, there is one exception to this relatively normal pattern: $\nu(SO_2)_{as}$ for $[Br(SO_3F)_2]^+$ is unexpectedly high and found at 1500 cm^{-1}. Even though the asymmetric SO_2 stretch has been found previously in this region for SO_3F derivatives like FSO_3F,[10] $S_2O_6F_2$,[10] and $S_2O_5F_2$,[11] these compounds are not strictly comparable to $[Br(SO_3F)_2]^+$, as is evident from the position of the remaining two SO stretching modes. The same unusual behavior had been found previously in the Raman spectrum of $Br(SO_3F)_3$[4] with the highest SO stretch at 1490 cm^{-1}.

From a comparison of the Raman spectra listed in Table II it appears that the bands in the region of 640–750 cm^{-1} are not found for the potassium salt and are most likely due to the $[Hal(SO_3F)_2]^+$ ion. Since both SO_3F stretching and deformation modes are generally not found in this region and are rarely so intense, assignment of these bands as halogen–oxygen skeletal vibrations is plausible. The following assignment is suggested: $\nu(BrO_2)_{as}$ at 745 cm^{-1} and $\nu(BrO_2)_s$ at 652 and 640 cm^{-1}; $\nu(IO_2)_{as}$ at 712 and 690 cm^{-1} and $\nu(IO_2)_s$ at 663 and 650 cm^{-1}. The observed splittings of some of the modes may be due to a slight nonequivalence of the two $[Hal(SO_3F)_2]^+$ ions in the cation. A band at 309 cm^{-1} for the bromine compound and at 284 cm^{-1} for the iodine compounds may be the BrO_2 or the IO_2 bending mode, respectively. These assignments of the Br–O and I–O skeletal vibrations suggest that our previous[4] assignments of these vibrations in $I(SO_3F)_3$ and $Br(SO_3F)_3$ are probably too low and should be revised.

All bands in the lower frequency range are not distinguishable from the anion vibrations, perhaps with the exception of the bending mode at ~625 cm^{-1} which is also present in $[I(SO_3F)_4]^-$. The Raman bands at 308, 462, and 1242 cm^{-1} reported by Gillespie and Morton[7] for solutions of $Br(SO_3F)_3$ in superacid and ascribed to the $[Br(SO_3F)_2]^+$ cation are all observed as strong bands for solid $[Br(SO_3F)_2]_2[Sn(SO_3F)_6]$ in approximately the same region.

Experimental Section

The chemicals $S_2O_6F_2$,[12] $Sn(SO_3F)_4$,[9,13] $I(SO_3F)_3$,[1] and $BrSO_3F$[3] were synthesized according to published methods. Raman spectra were obtained on a Cary 81 spectrometer equipped with a Spectra Physics Model 125 He–Ne Laser. The samples were contained in flat-bottom Pyrex tubes (5-mm o.d.) Solids were handled in a "Dri-Lab", Model No. HE-re-2 (Vacuum Atmospheric Corp.), filled with purified dry nitrogen and equipped with a "Dri-Train", Model No. HE-93 B. The Mössbauer spectrometer has been described elsewhere.[9]

All synthetic reactions were carried out in Pyrex reactors of ~100-ml volume, equipped with Teflon stem valves and Teflon-coated magnetic stirring bars. Generally 10–20 ml of $S_2O_6F_2$ was added to the reaction mixture by vacuum distillation. Details of the synthesis are given in the Discussion. The solid materials were obtained after removal of the solvent. In the case of $[I(SO_3F)_2]_2[Sn(SO_3F)_6]$ a yellowish liquid mass was formed initially which solidified only after 3–5 days.

Characterization of the Compounds. $[I(SO_3F)_2]_2[Sn(SO_3F)_6]$ is a yellowish white, very hygroscopic solid (mp 74–75 °C). Quantitative analysis was performed by Alfred Bernhardt, Elbach, West Germany. Anal. Calcd: I, 18.63; S, 23.49; F, 13.87. Found: I, 18.77; S, 23.53; F, 14.23.

$[Br(SO_3F)_2]_2[Sn(SO_3F)_6]$ is a pale yellow to white, very hygroscopic solid, melting to a yellow liquid at 48–50 °C. Anal. Calcd: Br, 12.60; S, 25.22; F, 14.90. Found: Br, 12.86; S, 25.47; F, 15.15.

Acknowledgment. Financial support from the National Research Council of Canada is gratefully acknowledged.

Registry No. $[I(SO_3F)_2]_2[Sn(SO_3F)_6]$, 58718-63-1; $[Br(SO_3F)_2]_2[Sn(SO_3F)_6]$, 58718-64-2; $Sn(SO_3F)_4 \cdot 2BrSO_3F$, 58718-65-3; $I(SO_3F)_3$, 13709-37-0; $Sn(SO_3F)_4$, 28017-03-0.

References and Notes

(1) J. R. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 354 (1960).
(2) F. Aubke and G. H. Cady, *Inorg. Chem.*, **4**, 269 (1965).
(3) F. Aubke and R. J. Gillespie, *Inorg. Chem.*, **7**, 599 (1968).
(4) H. A. Carter, S. P. L. Jones, and F. Aubke, *Inorg. Chem.*, **9**, 2485 (1970).
(5) M. Lustig and G. H. Cady, *Inorg. Chem.*, **1**, 714 (1962).
(6) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1236 (1966).
(7) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, **11**, 586 (1972).
(8) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **12**, 328 (1973).
(9) P. A. Yeats, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc. A*, 2188 (1970).
(10) A. M. Qureshi, L. E. Levchuk, and F. Aubke, *Can. J. Chem.*, **49**, 2544 (1971).
(11) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2179 (1961).
(12) G. H. Cady and J. M. Shreeve, *Inorg. Synth.*, **7**, 124 (1963).
(13) The interaction of $SnCl_4$ with $S_2O_6F_2$ is rather vigorous and may lead occasionally to an explosion. It is advisable to warm the mixture rather carefully.

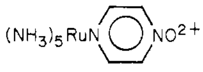
Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Reduction of Pyrazine Oxide, Free and Coordinated to Ruthenium(II)

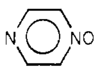
M. A. Blesa and H. Taube*

Received October 13, 1975 AIC50739B

Coordination of N_2O to Ru(II) enormously increases the rate of reduction of the oxide by V^{2+} or by Cr^{2+}.[1] A possible explanation of the effect is that Ru(II) assists in the reduction of the coordinated N_2O, with the internal and the external reducing agents cooperating in producing a $2e^-$ reduction of N_2O. On the basis of this hypothesis, it seemed reasonable to suppose that pyrazine oxide when coordinated to Ru(II) would also undergo reduction more rapidly than does free pyrazine oxide. Accordingly, we undertook to study the rate of reduction of both



and



The expected effect was not observed, and as a result our understanding of how Ru(II) enhances the reducibility of N_2O has not been much advanced. Because results we have obtained may nevertheless be of interest in other contexts, we make a brief report of them here.

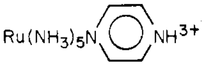
Experimental Section

Pyrazine oxide was prepared following the procedure described by Klein and Berkowitz.[2] The product obtained was recrystallized from benzene and then subjected to analysis. Anal. Calcd: C, 50.0; H, 4.2; N, 29.2. Found: C, 49.4; H, 4.23; N, 29.3. The ir and uv spectra agreed well with those described.[2]

The ion $Ru(NH_3)_5C_4H_4N_2O^{2+}$ was prepared by mixing $Ru(NH_3)_5OH_2^{2+}$ with pyrazine oxide, the former in 10% excess, under an atmosphere of argon. After complexation was complete, saturated sodium bromide was added. The solid was collected, washed, and dried. Anal. Calcd for $[Ru(NH_3)_5C_4H_4N_2O]Br_2$: C, 10.87; N, 22.18; H, 4.33; Br, 36.14. Found: C, 10.56; N, 21.97; H, 4.28; Br, 36.98.

Solutions containing V(II) and Cr(II) were prepared by standard procedures.

The spectrophotometric method was used in determining reaction rates. In all cases, experiments were done under pseudo-first-order conditions, with the reducing agent being used in excess. For V(II) in reaction with uncomplexed ligand, measurements were made at 214 nm; this wavelength is at a band maximum for pyrazine oxide, the product pyrazine showing much weaker absorption. Advantage was taken of the $\pi^* \leftarrow \pi d$ charge-transfer transition in measuring the rate of reduction of the complex of pyrazine oxide with Ru(II). The band maxima for the reactant complex and the product[3]



in acid solution coincide (λ 527 nm) but there is enough difference in the extinction coefficients to make it possible to follow the reaction using light in the visible region of the spectrum. With Cr^{2+} as reductant, reaction is too rapid for the rate to be measured by ordinary