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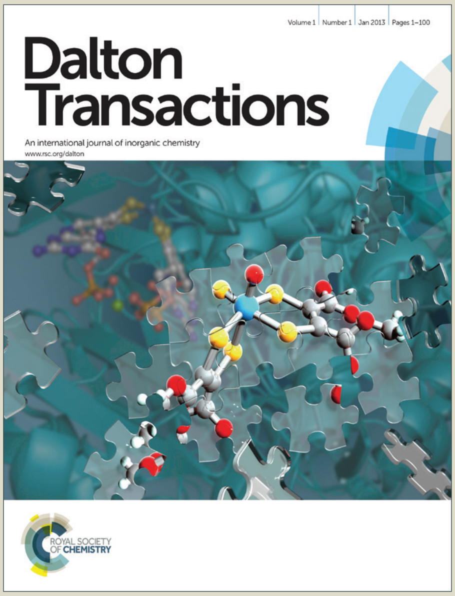

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A 2,2’-bipyridine coordination complex of $[ICl_2]^+$

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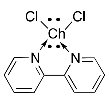
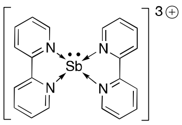
The formation of a new class of I(III) compound is reported; an N,N’ chelated iodine cation ($[bpy\text{-}ICl_2]^+$; bpy = 2,2’-bipyridine). The complex is obtained as an $[ICl_4]^-$ salt and is formed via simple reaction of bpy with ICl_3. The compound is relatively unstable, but may be stored as a solid and is shown to be competent in the oxidative chlorination of Au(I)-NHC complexes.

2,2’-Bipyridine (bpy) is one of the classic ligands in coordination chemistry. It might therefore be expected that little would be left to investigate in the simple, fundamental coordination chemistry of this ligand with inorganic elements. However, for the heavier atoms of the p-block recent years have seen a good deal of activity in the exploration of new bpy complexes. For example, the first bpy complexes with Se and Te (**1Ch**) were only reported as late as 2009.[1] Here bpy was used to sequester unstable $SeCl_2$ or completely inaccessible $TeCl_2$ in a “bottleable” solid form. The $TeCl_2$-bpy complex (**1Te**) has subsequently been used as a convenient source of electrophilic Te(II) to generate Te centred polycations and functionalized tellurophenes.[2-4] For group 15, bpy has ben used to generate polycationic Sb (**2**), As (**3**) and Bi complexes featuring novel bonding at these elements.[5-7] Burford has also recently used bpy to investigate the coordination chemistry of Me_2ECl_2 type compounds from group 14 (**4E**).[8]



1Ch; Ch = Se, Te



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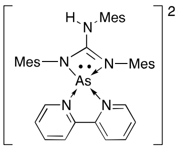

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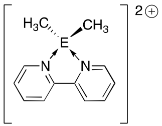
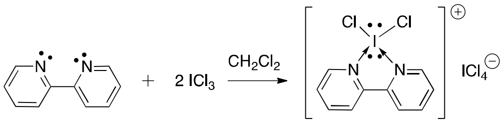


4E; E = Si, Ge, Sn

Here we report on the synthesis of a new type of iodine(III) compound – a square planar $[ICl_2]^+$ cation stabilized by bpy, via a straightforward synthesis from ICl_3. An investigation of the electronic structure was undertaken and preliminary investigation of the chemistry of this compound is also described, demonstrating that it is a powerful oxidant.

The 1:2 stoichiometric reaction of bpy with ICl_3 in CH_2Cl_2 (Scheme 1) resulted in the immediate formation of a bright yellow precipitate. The mixture was centrifuged, the precipitate washed with Et_2O and briefly dried *in vacuo*. The powder was sparingly soluble in $CDCl_3$. ^1H NMR spectroscopy revealed one bpy containing product with the most downfield bpy signal exhibiting a resonance at 8.94 ppm in $CDCl_3$, which is similar to that observed for bipy-$SeBr_2$ in the same solvents.[1] The NMR sample was cooled to -40 °C overnight resulting in the formation of single crystals. X-ray diffraction analysis on the crystals revealed the compound to be the bpy adduct of $[ICl_2]^+$ as an $[ICl_4]^-$ salt (**5,** Figure 1). It should be noted that the crystals were highly sensitive to ambient conditions, decomposing in less than one minute in Paratone N oil that had been stored over Na metal. Compound **5** is isolated in 54% yield from the reaction. There are a few older reports of the reactivity of ICl_3 with pyridine ligands forming complexes of various proposed stoichiometries, using melting points as the primary characterization method. Formation of $[pyr\text{-}ICl_2]^+$ species were proposed but not structurally verified.[9, 10] The formation of the $[ICl_4]^-$ anion in **5** is a result of ligand-induced ionization, which has recently been identified as a feature of main group halide coordination chemistry, specifically for $GeCl_2$ and $SnCl_2$.[11]



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Scheme 1 Synthesis of compound 5.

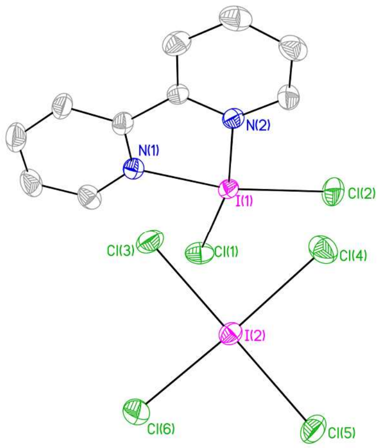


Figure 1. Solid-state structure of compound **5**. Selected bond distances (Å) and angles(°) (B3LYP/def2-TZVP calculated values in []): I(1)-N(1) 2.282(3) [2.427], I(1)-N(2) 2.267(3) [2.427], I(1)-Cl(1) 2.472(1) [2.417], I(1)-Cl(2) 2.445(1) [2.417], N(1)-I(1)-N(2) 72.1(1) [68.4], N(1)-I(1)-Cl(2) 166.39(8) [163.8], Cl(1)-I(1)-Cl(2) 99.47(4) [100.8], N(1)-I(1)-Cl(1) 94.06(7) [95.4]

Compound **5** is very sensitive to being dissolved in MeCN, where conversion of **5** into protonated bpy was observed to happen within minutes by ^{1}H NMR, with complete conversion in about one hour. A freshly prepared sample of **5** in CH_3CN placed in the glovebox freezer resulted in the growth of the same single crystals of **5** as were obtained from $CDCl_3$. However, if crystallization was attempted at room temperature and left undisturbed, single crystals of protonated bpy as an $[ICl_2]^-$ salt were formed. Prolonged handling (hours) in CH_2Cl_2 or $CDCl_3$ solution resulted in the formation of **6** (Scheme 2) and protonated bpy as an $[ICl_2]^-$ salt, as ascertained by a combination of ^{1}H NMR spectroscopy and X-ray crystallography.

The origin of the proton in the bpy salt product cannot be easily explained. Observation of the decomposition in CD_3CN rules out a solvent origin in acetonitrile as a distinct proton is observed. While adventitious water cannot be conclusively ruled out, every effort was taken to rigorously exclude water. An FT-IR spectrum (as a KBr pellet) of freshly produced solid **5** handled under a strictly inert atmosphere shows no evidence of a N-H stretch in the spectrum. If the same sample is prepared in the ambient atmosphere of the lab, a distinct N-H stretch band arises that is consistent with protonated bpy at $\nu = 3163$ cm^{-1}.[12] We therefore believe that solid **5** initially obtained in the reaction of bpy with ICl_3 is free of protonated bpy, which is subsequently formed by decomposition of **5** when it is held in solution or exposed to ambient conditions. The ^{1}H NMR spectrum of protonated bpy generated from bpy and one equivalent of ethereal HCl is given in the supporting information for comparison.

To summarize, compound **5** is stable if stored as a solid below -40°C under N_2 and should be promptly isolated from the initial reaction as handling, especially in solution, causes ready formation of protonated bpy and redox products ($[ICl_2]^-$).

The square planar geometry about the iodine centre in **5** indicates that the +3 oxidation state has been retained for iodine. This is an important observation, as spontaneous reduction processes with elimination o X_2 (X = Cl, Br, I) involving main group halides reacted with Lewis bases have been observed in several cases, and +3 is an unusually high oxidation state for iodine.[13-18] The iodine-nitrogen bond distances in **5** are 2.282(3) and 2.267(3) Å for I(1)-N(1) and I(1)-N(2), respectively. These distances are longer than those in T-shaped I(III) dication $[Ph\text{-}I(pyridine)_2]^{2+}$, which are approximately 2.20 Å.[19] There are very few other crystallographically characterized complexes in which bpy or related N,N' ligands chelate an iodine atom. In the bpy complex of $C_6F_5\text{-}IF_2$ the I-N bond distances are 2.79 Å.[20] In the related 1,10-phenanthroline complex to $C_6F_5\text{-}IF_2$ from the same report they are 2.81 Å. The 1,10-phenanthroline complex of $[Ph_2I]^+$ has I-N bond distances of 2.92 and 3.16 Å.[21] For reference the sum of the van der Waals radii for I and N is 3.53 Å and the sum of the covalent radii is 2.08 Å.[22] The I-N bond distances in **5** represent substantially shorter bonds, which are closer to the sum of covalent radii than any previously structurally verified N,N chelated iodine compounds. There is a report of a bpy complex of I(V), with bpy stabilizing the $[PhI{=}O]^{2+}$ dication. The ^{1}H NMR shift for the most downfield bpy signal is strongly deshielded (9.18 ppm in $CDCl_3$), likely indicating a strong interaction with the iodine, but this complex was not structurally characterized.[23] The I-Cl distances in the cation range from 2.445 to 2.472 Å. These can be compared to a range of 2.462-2.532 Å in the $[ICl_4]^-$ anion, and are typical for I-Cl.

B3LYP/def2-TZVP optimized bond distances for **5** (without the ICl_4^- counterion) yield a structure of C_{2v} symmetry with I-N and I-Cl bond distances of 2.403 and 2.418 Å, respectively. While the I-Cl bond distances are very similar to the experimental parameters, the I-N distance is 0.1-0.15Å greater. For the $C_6F_5\text{-}IF_2$ bpy complex, the I-N bond is calculated to be 2.978 Å, again about 0.15 Å greater than the experimental value. The deviation likely arises from the omission of packing effects and the increased symmetry in the calculations.

As compound **5** is a unique type of iodine-based coordination complex, a more detailed computational investigation of the bonding was undertaken, with a particular focus on the I-N bonding. The I-N σ bonding interaction is relatively high in energy and can be found in the HOMO-2 of the complex, with σ* interactions found in the LUMO+1 and LUMO+2. The HOMO is π symmetric, and centred on the ICl_2^+ fragment, while the LUMO is π symmetric and ligand based (Figure 2).

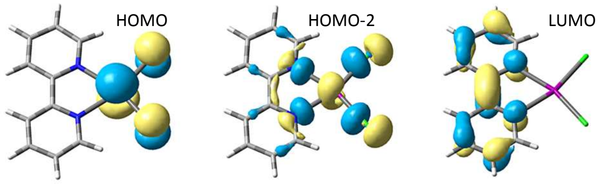


Figure 2. Important frontier molecular orbitals of compound **5**.

Energy decomposition analysis (EDA) was used to further probe the nature of the I-N bonds, with results presented in Table 1. For the cation in **5**, EDA analysis indicates that the interaction of bpy and ICl_2^+ is composed of 49.8% electrostatic (ΔE_{elstat}) and 50.2% covalent orbital (ΔE_{orb}) contributions. That result is almost identical to the prototypical iodine-nitrogen coordination complex, the bispyridine iodonium cation ($[pyr\text{-}I\text{-}pyr]^+$), with I-N bonds of 2.25 Å, that was characterised as a donor-acceptor bond.[24] Use of the X-ray geometry for **5**, with shortened I-N bonds as compared to the optimized geometry had very little effect on the EDA results. It is concluded that the I-N bonding in **5** exhibits significant donor-acceptor (dative) character, although the strength of the interaction (-340.0 kJ/mol) is only half that of the ($[pyr\text{-}I\text{-}pyr]^+$ complex (-736.4 kJ/mol). In comparison, EDA analysis of the bpy complex of $C_6F_5\text{-}IF_2$ (I-N bond distance of 2.79 Å)[20] indicates that the I-N bond is predominantly electrostatic (62.5%), which is further reflected in the significantly smaller interaction energy (-64.9 kJ/mol).

Table 1. Results of the EDA calculations at BP86/TZ2P (kJ/mol).

	5	$[IPyr_2]^+$	$C_6F_5IF_2$-bpy
Symmetry	C_{2v}	D_{2d}	C_2
ΔE_{int}	-340.0	-736.4	-64.9
ΔE_{Pauli}	592.0	645.9	135.4
$\Delta E_{Elstat}{}^a$	-463.7 (49.8)	-706.2 (51.1)	-125.2 (62.5)
$\Delta E_{orb}{}^a$	-468.3 (50.2)	-676.1 (48.9)	-75.1 (37.5)
$\Delta E_{a1}{}^b$	-232.1 (49.6)	-104.4 (15.4)	-47.1 (62.8)
$\Delta E_{a2}{}^b$	-27.9 (6.0)	-7.9 (1.2)	
$\Delta E_{b1}{}^b$	-35.9 (7.7)	-8.3 (1.2)	
$\Delta E_{b2}{}^b$	-172.4 (36.8)	-432.7 (64.0)	
$\Delta E_{e1}{}^b$		-122.7 (18.2)	-27.9 (37.2)

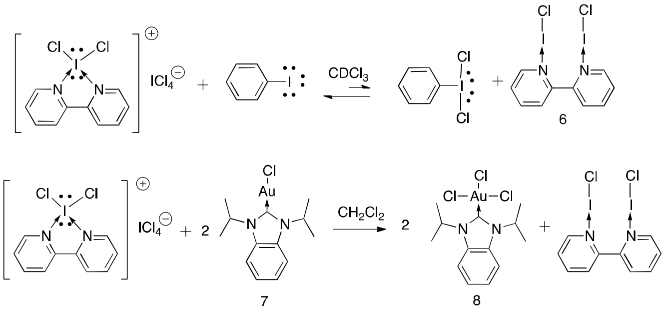
[a] The values in parentheses are the percentage contributions to the total attractive interactions $\Delta E_{elsat} + \Delta E_{orb}$.

[b] The values in parentheses are the percentage contributions to the total orbital interactions ΔE_{orb}. For $C_6F_5IF_2$-bpy (C_2 symmetry), ΔE_{a1} refers to a symmetry (ΔE_a) and ΔE_{e1} refers to b symmetry (ΔE_b).

The breakdown of the orbital contribution (ΔE_{orb}) indicates that σ orbitals contribute the majority of the covalent interaction (in D_{2d} and C_{2v} symmetry the $\sigma(p_z)$ contributions are included in ΔE_{b2}, whereas in C_2 symmetry they are included in ΔE_{a1}). The EDA-NOCV method allows analysis of individual orbital interactions that comprise ΔE_{orb}. For **5**, there are only two major contributions, which comprise 76.2% (-356.7 kJ/mol) of ΔE_{orb}; both arise from bpy→ICl_2^+ σ donation. The third contribution (-25.5 kJ/mol, 5.4% of ΔE_{orb}) includes a measure to π back-bonding, although donation comes from both the I atom and adjacent bpy ring carbon atoms. That is, there is only minimal π back-bonding between the iodine and bpy fragments (with a contribution to ΔE_{orb} of ~2-3%), as expected for poorly π-accepting pyridine rings. For the $C_6F_5\text{-}IF_2$ bpy complex, there are two weak (-55.1 kJ/mol) donor-acceptor interactions that contribute 73.4% of ΔE_{orb}. In a similar manner, π back-bonding only contributes to ~2-3% of the orbital interaction.

The use of a dative model to represent adducts of electronegative main group cations with typical ligands has attracted criticism.[25] For example, a tris-cyclopropylidene carbene adduct of "N^{3+}" was represented as a nitrogen trication stabilized by three carbene ligands. However, the NPA charge on the N center was calculated to be –0.45, in opposition to the +3 formal charge in the dative model.[26] Iodine is an electronegative element that is underrepresented in coordination chemistry. In the case of the cation in **5** the formal charge of +1 on the iodine atom in the dative model is in good agreement with the calculated NPA charge of +1.16. Indeed, iodine is the least electronegative element of I, N and Cl, and could therefore be considered to be acting as any other Lewis acidic metal in the bpy adduct presented here.

Dichloroiodobenzene ($PhICl_2$) is a convenient source of Cl_2, and as such is a common oxidizing agent in both organic and inorganic chemistry.[27,28] To gain an estimate of the chemical oxidative ability of **5**, it was reacted with PhI (Scheme 2) alongside comparisons with related I(III) compounds ICl_3, and $[ICl_4]^-$ as an $[nBu_4]^+$ salt. Reactions were performed *in situ* in $CDCl_3$ and monitored by ^1H NMR spectroscopy. The PhI:$PhICl_2$ ratio was then used as an estimate of the oxidative capacity. The reaction of ICl_3 with PhI resulted in a 0.37:0.56 ratio of PhI:$PhICl_2$, indicating that ICl_3 and $PhICl_2$ have similar oxidative capacities. Reaction of PhI with $[nBu_4][ICl_4]$ gave a 0.98:0.02 ratio of PhI:$PhICl_2$, demonstrating that $[ICl_4]^-$ is significantly less oxidizing than $PhICl_2$. Reaction of **5** with PhI resulted in a PhI:$PhICl_2$ ratio of 0.85:0.15, indicating that **5** is also less oxidizing than $PhICl_2$. The observed bpy signals in the spectrum were consistent with **6**, the bis-ICl adduct of bpy.[29] Based on the appearance of this complex, both the cation and anion in **5** must be involved. The low reactivity of $[ICl_4]^-$ observed in the control experiment led us to hypothesise that the cation in **5** is the better oxidizing agent, producing a transient $[bpy\text{-}I]^+$ species that abstracts a chloride from $[ICl_4]^-$ giving ICl_3, which can subsequently react with PhI in its typical fashion, with the resulting ICl giving the observed bis-ICl bpy complex. The equilibrium for this reaction clearly lies on the side of the reactants. A further control reaction showed that use of **6** itself results in no chlorination of PhI.



Scheme 2. Oxidative reactivity of compound 5.

Hypervalent chlorinated iodine compounds, most commonly $PhICl_2$, have also been regularly used in the oxidative chlorination of late transition metals, particularly Pd, Pt and Au.[30-35] The oxidative efficacy of compound **5** was tested by reacting it with NHC-Au(I)-Cl (**7**, Scheme 2), which was selected since its oxidation with $PhICl_2$ has been reported and therefore comparisons can be readily made. The reported reaction gave a 99% isolated yield of the Au(III) complex.[35] A 1:2 stoichiometric reaction of **5** with **7** (allowing for both the cation and anion to react) was allowed to stir for 5 minutes as an NMR scale reaction in $CDCl_3$. The major products that could be identified were Au(III) complex **8** and I(I) product **6**. Single crystals grown from the NMR sample confirmed production of **8** via a unit cell comparison. Control reactions on NMR scales in $CDCl_3$ showed that both free ICl_3 and $[ICl_4]^-$ (as a $[^nBu_4N]^+$ salt) also resulted in complete oxidation of **7**. A scaled up reaction in CH_2Cl_2 between **5** and **7** allowed for isolation of **8** in 75% yield, which is somewhat lower than the reaction with $PhICl_2$. However, this relatively high yield points to **5** remaining intact as the proposed compound, having been stored in the solid state at low temperature.

Conclusions

We have reported the first structurally verified example of a stabilized $[ICl_2]^+$ fragment (**5**). Compound **5** also represents the first N,N' chelate complex of iodine with a reasonably strong I-N bond, having an I-N bond distance of at least 0.5 Å shorter than other reported examples.[20] Computational analysis shows a much greater orbital interaction in our compound, consistent with a dative bond, rather than a charge transfer complex. Compound **5** is demonstrated to be a competent oxidant, with both the cation and anion active for oxidation. However, the instability of **5** does present a significant challenge. We are currently attempting to address this by generating a derivative containing a different anion, as well as exploring the effect of other N,N' ligands on the stability of the $[ICl_2]^+$ complex. We thank the La Trobe Institute of Molecular Sciences and La Trobe University for their generous funding of this work. The Victorian Partnership for Advanced Computing (VPAC), the National Computational Infrastructure National Facility (NCI-NF) and La Trobe University are acknowledged for substantial computing resources. This project is also supported by an ARC DECRA award (JLD; DE130100186).

Notes and references

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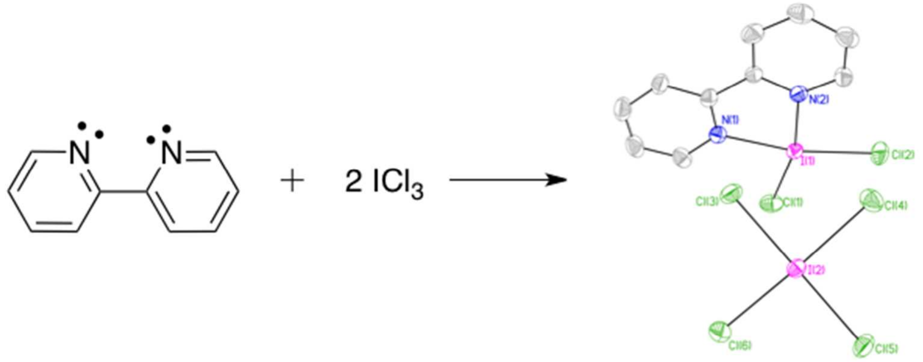
Electronic Supplementary Information (ESI) available: Experimental procedures, X-ray crystallographic details, computational details, Cartesian coordinates of calculated geometries, EDA-NOCV analysis. For X-ray crystallographic details in .cif format see CCDC 1025434 (**5**), 1025435 ([bipy-H]$[ICl_2]$) and 1032987 ($[^nBu_4N][ICl_4]$). See DOI: 10.1039/c000000x/

1. J. L. Dutton, G. J. Farrar, M. J. Sgro, T. L. Battista and P. J. Ragogna, *Chem. Eur. J.*, 2009, **15**, 10263-10271.
2. J. L. Dutton and P. J. Ragogna, *Chem. Eur. J.*, 2010, **16**, 12454-12461.
3. G. He, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360-5363.
4. G. He, W. T. Delgado, D. J. Schatz, C. Merten, A. Mohammadpour, L. Mayr, M. J. Ferguson, R. McDonald, A. Brown, K. Shankar and E. Rivard, *Angew. Chem. Int. Ed.*, 2014, **53**, 4587-4591.
5. A. L. Brazeau, A. S. Nikouline and P. J. Ragogna, *Chem. Commun.*, 2011, **47**, 4817-4819.
6. S. S. Chitnis, N. Burford and M. J. Ferguson, *Angew. Chem. Int. Ed.*, 2013, **52**, 2042-2045.
7. A. P. M. Robertson, N. Burford, R. McDonald and M. J. Ferguson, *Angew. Chem. Int. Ed.*, 2014, **53**, 3480-3483.
8. A. P. M. Robertson, J. N. Friedmann, H. A. Jenkins and N. Burford, *Chem. Commun.*, 2014, **50**, 7979-7981.
9. R. D. Whitaker, J. R. Ambrose and C. W. Hickman, *J. Inorg. Nucl. Chem.*, 1960, **17**, 254-256.
10. R. D. Whitaker and J. R. Ambrose, *J. Inorg. Nucl. Chem.*, 1962, **24**, 285-289.
11. A. P. Singh, H. W. Roesky, E. Carl, D. Stalke, J. Demers and A. Lange, *J. Am. Chem. Soc.*, 2012, **134**, 4998-5003.
12. P. K. Bakshi, T. S. Cameron and O. Knop, *Can. J. Chem.*, 1996, **74**, 201-220.
13. J. L. Dutton, R. Tabeshi, M. C. Jennings, A. Lough and P. J. Ragogna, *Inorg. Chem.*, 2007, **46**, 8594-8602.
14. B. D. Ellis, M. Carlesimo and C. L. B. Macdonald, *Chem. Commun.*, 2003, 1946-1947.
15. B. D. Ellis, C. A. Dyker, A. Decken and C. L. B. Macdonald, *Chem. Commun.*, 2005, 1965-1967.
16. J. L. Dutton, A. Sutrisno, R. W. Shurko and P. J. Ragogna, *Dalton Trans.*, 2008, 3470-3477.
17. G. Reeske and A. H. Cowley, *Chem. Commun.*, 2006, 4856-4858.
18. N. Kuhn, A. Abu-Rayyan, C. Piludu and M. Steimann, *Heteroatom Chem.*, 2005, **16**, 316-319.
19. T. P. Pell, S. A. Couchman, S. Ibrahim, D. J. D. Wilson, B. J. Smith, P. J. Barnard and J. L. Dutton, *Inorg. Chem.*, 2012, **51**, 13034-13040.
20. H. Frohn, M. E. Hirschberg, U. Westphal, U. Florke, R. Boese and D. Blaser, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2249-2257.
21. M. Ochiai, T. Suefuji, K. Miyamoto and M. Shiro, *Chem. Commun.*, 2003, 1438-1439.
22. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.
23. V. V. Zhdankin, A. Y. Koposov and N. V. Yashin, *Tet. Lett.*, 2002, **43**, 5735-5737.
24. D. C. Georgiou, P. Butler, E. C. Browne, D. J. D. Wilson and J. L. Dutton, *Aust. J. Chem.*, 2013, **66**, 1179-1188.
25. D. Himmel, I. Krossing and A. Schnepf, *Angew. Chem. Int. Ed.*, 2014, **53**, 6040-6046.
26. A. Kozma, G. Gopakumar, C. Fares, W. Thiel and M. Alcarazo, *Chem. Eur. J.*, 2013, **19**, 3542-3546.
27. V. V. Zhdankin, *ARKIVOC*, 2009, 1-62.
28. For an extremely comprehensive book covering developments of hypervalent iodine compounds, both historical and recent see: V. V. Zhdankin, Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds, 2013, Wiley.
29. A. S. Batsanov, J. A. K. Howard, A. P. Lightfoot, S. J. R. Twiddle and A. Whiting, *Eur. J. Org. Chem.*, 2005, 1876-1883.
30. P. L. Arnold, M. S. Sanford and S. M. Pearson, *J. Am. Chem. Soc.*, 2009, **131**, 13912-13913.
31. J. M. Racowski, N. D. Ball and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 18022-18025.
32. M. Hofer and C. Nevado, *Eur. J. Inorg. Chem.*, 2012, 1338-1341.
33. M. Hofer and C. Nevado, *Tetrahedron*, 2013, **69**, 5751-5757.
34. S. Orbisaglia, B. Jacques, P. Braunstein, D. Hueber, P. Pale, A. Blanc and P. Fremont, *Organometallics*, 2013, **32**, 4153-4164.
35. H. Sivaram, J. Tan and H. V. Huynh, *Organometallics*, 2012, **31**, 5875-5883.



A straightforward synthesis of a new type of iodine(III) complex is presented – an N'N chelated $[ICl_2]^+$ cation.